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THE Association was organized in Boston, Mass., on June 21, 1882, with the object of providing its members with means of social intercourse and for the exchange of knowledge pertaining to the construction and management of water works. From an original membership of only TWENTY-SEVEN, its growth has prospered until now it includes the names of 800 men. Its membership is divided into six classes, viz.:

A Member shall be an officer or employee of a public or private water works, an engineer, chemist or other person qualified to aid or interested in the advancement of knowledge relative to water works.

An Honorary Member shall be a person of acknowledged eminence in some branch of water supply or of engineering.

A Junior shall be not less than eighteen years nor more than twenty-five years of age, a student or connected with water supply work.

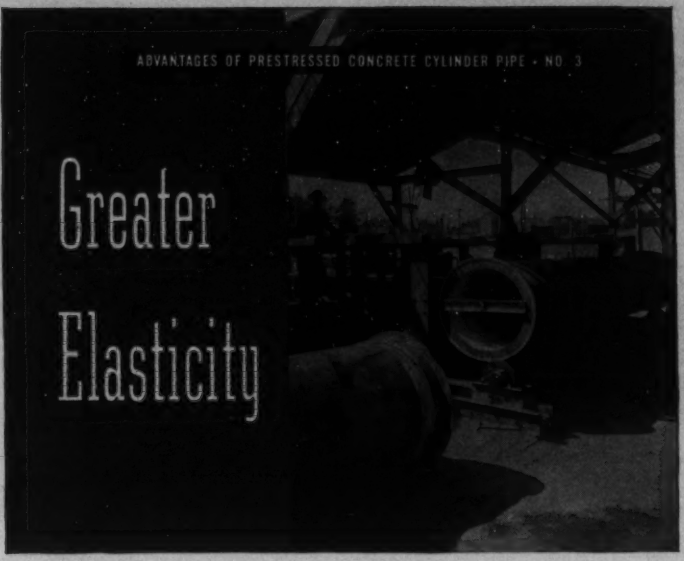
An Associate shall be either a person, firm or corporation engaged in manufacturing or furnishing materials or supplies for the construction or maintenance of water works.

A Corporate Member shall be either a Water Board, Commission, Company or Municipal Corporation.

The initiation fees and annual dues are as follows:

	Initiation Fee		*Annual Dues*
Members	$ 1.00	Members	$ 6.00
Juniors	1.00	Juniors	3.00
Associates	10.00	Associates	20.00
Corporate Members	10.00	Corporate Members	10.00

This Association has at least eight regular meetings each year, of which five are held in Boston, one in northern New England, one in southern New England, and one, the annual convention, held in September on such date as the Executive Committee may designate.



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Complete the last line of this jingle

Water works systems should not be neglected,
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The mounting deficit makes taxpayers cry.
100% metering is the only fair way,

This one's a snap—the only meter you need to understand is found in poetry. Study the tips listed on this page. Then write an informative last line for the jingle. As an example, the missing line could read:

"To charge consumers, make water plants pay."

You can submit as many last lines as you wish.

PRIZE LIST

1st Prize—$500.00	3rd Prize—$100.00	10 Consolation Prizes
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CONTESTS CLOSE AUGUST 31, 1946

CONTEST NO. 2

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1st Prize—$500.00	3rd Prize—$100.00	10 Consolation Prizes
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THESE *Water Works* AUTHORITIES WILL JUDGE ALL ENTRIES

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WILLIAM W. BRUSH, Editor of *Water Works Engineering*; former Chief Engineer, Bureau of Water Supply, Greater New York. Past President of A. W. W. A. Graduate of New York University.

ALBERT E. PAXTON, Publisher of *Engineering News-Record*. Vice President of the Water and Sewage Works Manufacturers Association. Graduate of Univ. of Illinois.

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All entries must be accompanied by coupon clipped from any contest announcement. Only one coupon is required to identify a contestant who submits a number of entries at the same time.

Write on one side of paper only. *DO NOT* put name or address on any entry. An executed coupon will serve as contestant's identification. Contests close August 31, 1946. Entries must be postmarked on or before that date.

Winners names in both contests will be posted in Pittsburgh-Empire Meter exhibit booths at the fall water works conventions. Checks will be mailed to winning contestants immediately upon completion of judging.

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Meters produce added revenue, usually enough to cover initial investment, maintenance costs and depreciation.

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CONTEST NO. 1 ☐ CONTEST NO. 2 ☐
Check in boxes provided. Where entries are submitted in both contests, check both boxes.

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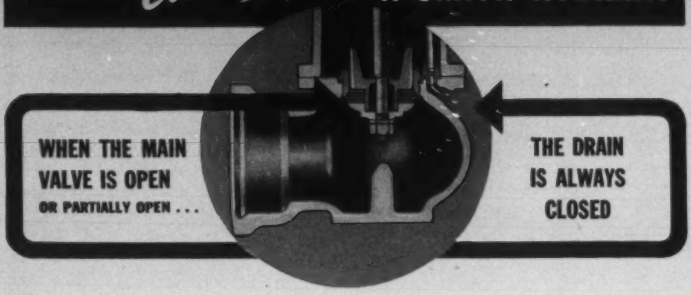
LEAKAGE THRU DRAIN *can never undermine* A SMITH HYDRANT



The Smith Fire Hydrant is so designed that the drain is open only when the main valve is completely closed. Water under pressure cannot pass through the drain in the event that the main valve is improperly closed or partially open.

16

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GATE VALVES
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TAPPING SLEEVES AND VALVES
WATER SERVICE BRASS GOODS

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KEEPING UP with the trenching machine is common practice when the pipe being installed is Transite! Crews can unload and install this light-weight asbestos-cement pipe quickly . . . handle all but the larger sizes without the aid of mechanical handling equipment. The modern Simplex Coupling cuts assembly time to a minimum . . . assures tight, yet flexible joints.

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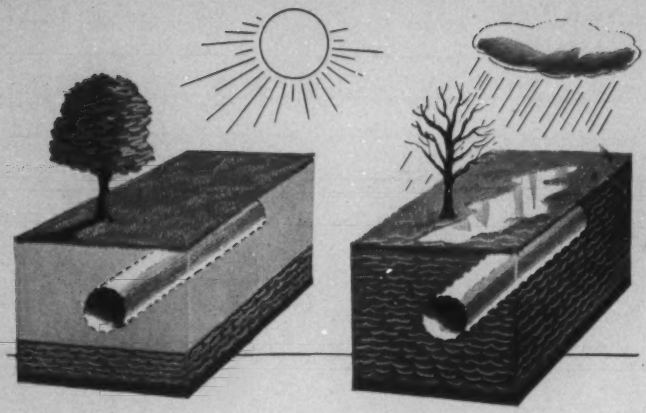

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Coal-tar Enamels, because of their ability to resist moisture absorption, provide constant, uniform and long-lasting STABLE insulation. They are not affected by the changing moisture content of soils, due to variation of seasons and weather conditions.

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A Mathews Hydrant can be turned to face any direction in the compass. This is due to the unique swivel flange at the base of the nozzle section. You simply loosen a few bolts . . . and turn the head with the minimum of labor and expense. And for the same reason, the number and size of the nozzle outlets can be changed by simply changing the head . . . without shutting the water off.

Take a look at the working parts—they are all contained in a removable barrel. In case something goes wrong, you unscrew the barrel from the elbow, lift it out, insert a spare. No digging or excavating; the pavement is intact; life and property are protected with almost no interruption at all; repair costs are held down. Mathews design is noteworthy throughout—oiling from the exterior; operating threads kept free of rust and dirt; frost-proof mechanism; protection case "Sand-Spun" for greater strength, elasticity, freedom from stresses. These and other features explain why there are so many Mathews hydrants in use everywhere in the world.

MATHEWS HYDRANTS

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MANUFACTURERS OF SAND SPUN PIPE (CENTRIFUGALLY CAST IN SAND MOLDS) AND R. D. WOOD GATE VALVES

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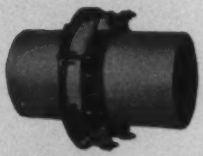

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Whatever type of pipe you may find in the hole—foreign or domestic, oversize or undersize, old or new—you can use a Dresser Style 60 Clamp without any delay *because it is adjustable to the exact pipe diameter.* You save time on the job—you get a better job. The special Dresser gasket keeps joint leakproof for life.

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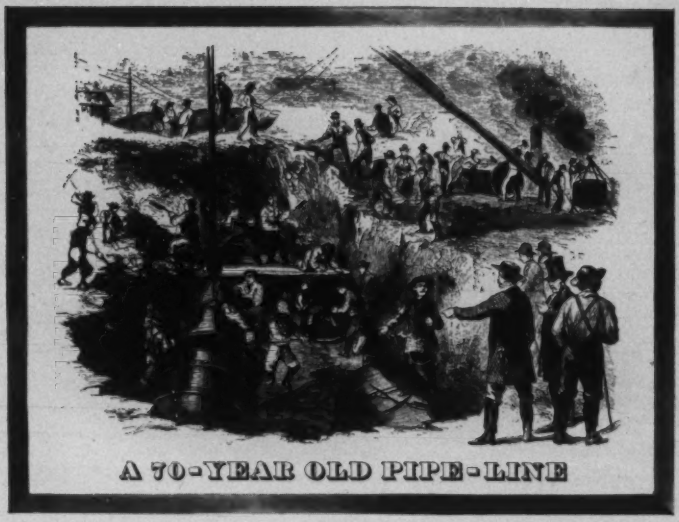

A 70-YEAR OLD PIPE-LINE

long abandoned...completely restored by Centriline

BACK IN THE YEAR 1874, over a hundred thousand feet of 24" and 36" wrought iron pipe were laid in the City of Rochester, New York — and continuously used until 1934. However, during the entire sixty years numerous repairs were made on this main until finally leakage became so great that this pipe-line had to be completely abandoned.

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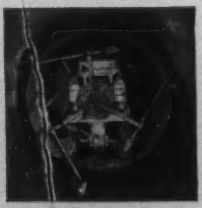
After cleaning, Centriline started to apply a sleek, new cement lining on September 12th, 1944 . . . and finished the job on November 22nd . . . in record breaking time. Furthermore, this old pipe-line which was abandoned ten years ago has been more than satisfactorily restored . . . because today its carrying capacity is higher than the original coefficient.



The Centriline process is a rapid and economical method of reconditioning pipelines of 30" or more. It consists of first cleaning the main and then applying by centrifugal force, a dense cement mortar lining of required thickness, mechanically troweled to a smooth finish. This is done underground, in place.

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Restores and Protects Pipe-Line Carrying Capacity

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New England Water Works Association
ORGANIZED 1882

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This Association, as a body, is not responsible for the statements or opinions of any of its members

COOLING-WATER BENEFITS FROM INCREASED RIVER FLOWS‡

BY M. LEBOSQUET, JR.*

[*Read September 11, 1945.*]

SINCE 1939 the U. S. Public Health Service has coöperated with the Corps of Engineers, U. S. Army, on investigations of surface-water pollution and allied problems in connection with proposed reservoirs to be built primarily for the purpose of storing flood waters and thereby reducing flood damage and suffering. The proposed reservoirs, however, may also be used for many other purposes, among which are the following: (1) power, (2) irrigation, (3) navigation, (4) domestic and industrial water supply, (5) recreation, (6) dilution water to assist in abating pollution, and (7) industrial cooling water. These reservoirs or impoundments are referred to as multiple-purpose projects.

The principal interest of the Water and Sanitation Investigations Station of the U. S. Public Health Service at Cincinnati is in item (6) above or, in other words, the possibility that impoundments will increase critical low flows to the benefit of water-pollution problems. Item (7), industrial cooling water, the subject of today's paper, is also considered by the U. S. Public Health Service. This interest is primarily an outgrowth of studies of water temperatures and their effect on water requirements for dilution of residual organic pollutants following various treatment processes.

The U. S. Public Health Service coöperation is concerned with four specific assignments within the two items (6) and (7) as follows:

(a) Estimates are made of desirable increases in minimum flows, in the interest of water-pollution abatement and cooling-water use. This activity involves computations of the oxygen sag in a stream below

‡Published with the approval of the U. S. Public Health Service.

*Sanitary Engineer, Water and Sanitation Investigations, Sanitary Engineering Division, U. S. Public Health Service, East Third and Kilgour Streets, Cincinnati, Ohio.

sources of pollution, plus computations of expected river-water temperatures made in accordance with methods to be outlined later.

(b) Evaluations are made of water-pollution abatement and cooling-water benefits from increased flow. In general, these evaluations are made on the basis of costs of treatment works necessary to accomplish improvement in stream conditions equivalent to those resulting from increased flow. Cooling-water benefits per unit reduction in temperature claimed by industrial engineers are normally accepted.

(c) Estimates are made of permissible decreases in greater-than-minimum flows. In general, lowering of the absolute minimum flow is highly undesirable and is seldom considered. Decreases in the higher flows, however, may be permissible in order to store water for seasonal uses such as irrigation, power and navigation. Such decreases are permissible only so long as sanitation needs are met.

(d) Studies are made of possible hazards resulting from impounding water of inferior quality.

The interest of the U. S. Public Health Service in the discharge of hot water has led into the field of thermodynamics, as such discharge involves the escape of excess heat from surface water to the atmosphere. Very little is available in the literature on the subject and it was necessary to devise methods of computation. One reference in "Mechanical Equipment of Buildings," Volume 2, by Harding and Willard, states that mill ponds may be designed on the basis of heat loss from a water surface of 4 BTU per square foot of surface area per hour per degree F. of difference in temperature between water and air. This basic reference was used as a starting point.

One result of the coöperative activity with the Corps of Engineers, or the U. S. Engineer Office, is a temperature formula which is used on each industrial problem. Results have been satisfactory. The principal purpose of this paper is to add this one formula to the collection available for use. The derivation is as follows:

K = Heat loss in BTU per sq ft per $^{\circ}F$ excess in temperature (of water over air) per hour;

L = Lb of water;

F = Excess temperature ($^{\circ}F$) of water over air at distance (D) in miles;

F_a = Initial excess temperature ($^{\circ}F$);

t = Time in hours;

A_s = Surface area—sq ft;
A_x = Cross-section area—sq ft;
h = Average depth of water—feet;
W = Average width of stream—feet;
MPH = Average velocity in miles per hour;
V = Average velocity in feet per second;
Q = Flow in cubic feet per second;
D = Distance in miles;

$$C = \frac{0.02347\ KW}{Q};$$

$$C' = 0.4343\ C;$$

$$BTU = {}^{\circ}F \times L;$$

$$^{\circ}F = \frac{BTU}{L}.$$

$$-dF = \frac{KA_sF}{L}\,dt$$

$$L/A_s = h \times 62.5, \qquad h = \frac{A_x}{W}$$

$$= \frac{A_x}{W} \times 62.5, \qquad A_x = \frac{Q}{V}$$

$$= \frac{Q \times 62.5}{W \times V}$$

$$t = \frac{D}{MPH} = \frac{D}{V \times \frac{60}{88}} = \frac{88\ D}{60\ V}$$

$$dt = \frac{88}{60\ V} \times dD$$

$$-dF = \frac{KFWV}{62.5\ Q}\,\frac{88}{60\ V}\,dD$$

$$= \frac{0.02347\ KW}{Q}\,FdD.$$

Substitute $C = \dfrac{0.02347\ KW}{Q}$

$$-dF = CF\,dD$$

$$\frac{-dF}{F} = C\,dD$$

$$-\int_{F_a}^{F}\frac{dF}{F} = C\int_{O}^{D} dD$$

$$-(Log_e F - Log_e F_a) = CD$$

$$Log_e F_a - Log_e F = CD$$

$$Log_e \frac{F_a}{F} = CD, \qquad \frac{F_a}{F} = e^{CD} = 10^{C'D}$$

$$F = F_a\, 10^{-C'D}$$

$$C' = 0.4343\, C = 0.4343 \times 0.02347\, \frac{KW}{Q}$$

$$= 0.0102\, \frac{KW}{Q}$$

$$F = F_a\, 10^{-0.0102\,\frac{KWD}{Q}} \tag{1}$$

$$F_a = \frac{BTU \text{ added per day}}{Q \times 5{,}400{,}000}, \qquad C'' = \frac{BTU \text{ added per day}}{5{,}400{,}000}$$

$$F_a = \frac{C''}{Q}$$

$$F = \frac{C''}{Q} \times 10^{-0.0102\,\frac{KWD}{Q}}. \tag{2}$$

Solving (1) for K:

$$Log_{10}\frac{F_a}{F} = C'D, \qquad C' = \frac{0.0102\,KW}{Q}$$

$$Log_{10}F_a - Log_{10}F = \frac{0.0102\,KWD}{Q}$$

$$K = \frac{Q\,Log_{10}\dfrac{F_a}{F}}{0.0102\,WD} \tag{3}$$

In applying the formula, it has been the practice to use averages. As there is a wide variation in hour-to-hour cooling-water use and resultant quantity of heat added to the stream, as well as changes in atmospheric conditions, there is little justification for refinements. Factors influencing the value of K have been investigated only to a minor extent. More heat is lost by rapid shallow streams than by slow sluggish streams, possible variations being from 18 to 6 BTU per square foot per hour per degree F. difference in temperature between water and air. In practice, values of K are derived from stream temperature readings and computations are then made of expected temperatures under new conditions.

It is to be noted that no item for time appears in the final formula. This means that, if the surface area (WD) is the same and the stream flow (Q) is the same, it makes little difference whether the stream is 2 ft deep or 20 ft deep. In the deep river, time between points will be much greater, but the volume of water to be cooled will be correspondingly greater. In other words, changing a shallow stream to a deep, possibly navigable channel will have little effect on resulting cooling-water temperatures, as long as the surface area is not increased.

Increasing stream flow results in two great benefits to cooling-water use. First, the water discharged from the plant will not increase the temperature of water taken in to as great an extent, because a greater portion of the cooling water taken from the stream will be fresh water rather than water that has already circulated through the plant. For example, a plant pumping 200 cfs from a stream with a flow of 50 cfs will pump 75% of its own discharge. Increased flows under such circumstances are very beneficial. The second great benefit is that the same BTU contribution per day raises the temperature of the larger volume of water to a lesser degree, to the benefit of the user downstream.

Strangely enough, the increased flow in certain ranges may not benefit all the downstream users. When streams are very low, the time of flow between users may be so great that the effect of the upper industry may be entirely lost. Increasing the flow under such circumstances may carry the hot water downstream before the heat is lost to the atmosphere.

If a curve is drawn with distance (D) as abscissa (W being constant) and excess temperature (F) as ordinate, a straight line is obtained on semi-logarithmic paper. Use can be made of this fact in graphical solutions.

In general, financial benefits from reduced cooling-water temperatures are not large enough to pay more than a small fraction of the cost of an impoundment. However, if an impoundment is planned for flood control, navigation and other uses, cooling-water benefits may be a worth-while additional justification for the project.

Temperature considerations are very important from a pollution standpoint. It is much more difficult to maintain aerobic conditions in a polluted hot stream than in one of normal temperature. Hot water can, therefore, in a sense, be considered as oxygen-depleting pollution. There have been several occasions to use stream temperature computations to help determine the effect of increased flow on pollution conditions in streams used for cooling purposes.

THE DEVELOPMENT OF PLASTIC COATINGS FOR CORROSION PROTECTION IN THE WATER-WORKS INDUSTRY

BY ARTHUR B. SMITH*

[*Read February 28, 1946.*]

To combat corrosion and contamination in the water-works industry, the field of plastics, after many years of research and development, stands ready today with time-proven systems of cold-applied, air-dried, thermoplastic protective coatings. These coatings are odorless, tasteless, chemically inert and resistant to cold mineral acids, are unaffected by alkalis, impervious to oils, fats, gasoline and mineral salts and are insoluble in alcohol and water. Based on synthetic organic resins, the coatings are also non-conductors of electric current and are resistant to electrolysis. They adhere tightly over a well prepared surface of steel, concrete or wood and present a smooth surface in colors that may well fit into any color scheme. They will withstand a remarkable amount of abrasion, yet are plastic enough not to crack, check or fracture. Thus, an economical and effective means of corrosion control for a large number of water-works installations is believed to have been found.

The automobile industry is believed to be one of the first, and is perhaps today one of the largest, users of plastic coatings. It was in the early 1920's that the plastic industry developed finishes which revolutionized automobile painting. Since that time research and development have greatly improved quality and reduced the cost of these finishes. Other large users of metal finishes soon found that surface coatings made from baked plastic resins were corrosion-proof, did not become chalky, retained a deep gloss and did not color with age. Such resins include phenol-formaldehyde, urea-formaldehyde and the alkyd resins. You will find them in use on your refrigerators, stoves and similar equipment. Most of these resins, however, are of the thermosetting type—that is, they require heat to bring on a protective film firmly bonded to the surface.

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Long has it been perceived that the best possibilities for an economic solution to corrosion and contamination problems in water works lay in a protective coating. Yet, to find a material that could easily be applied with a brush or spray gun, could be rapidly dried by air and still had all of the corrosion-resistant features presented quite an obstacle. So again, modern industrial designers delved into their never-ending research with plastics and came up with an apparent answer to an age-old problem.

It is from the drama of raw materials, such as limestone, petroleum, coal, water, air and salt, being transformed into basic materials, which are both water-resistant and resistant to most corrosive chemicals, that these new protective coatings are formulated, just as waste products, such as peanut shells, corn cobs, insect secretions and bits of cloth, have been transformed into radio cabinets, electrical equipment, jewelry and silk substitutes. Yes, among all the processes and products of creative chemistry, none has attracted more attention than plastics and none seems to stand out as being of greater interest or more universally useful to all industries than these surface coatings.

Surface coatings made from thermoplastic resins have the same chemical properties of molded products, made from the same resins, as do some of the phenol-formaldehyde type of thermosetting plastics. Yet, unlike such plastics, they require no heat to meet their maximum efficiency.

Most of the companies now in the plastic-coating field were organized during the war and the coatings were largely used as corrosion-resistant finishes in the marine, electrical and aircraft industries. However, a few companies had spent years of research, development and actual field testing prior to the war's beginning and had extended the coatings' uses far beyond these particular fields. Among these is the company which I represent. Our original objective was the determination of an efficient, air-dried, corrosion-resistant lining for concrete sewers, conduits, waterways, etc.

We are all aware that corrosion is one of the more important chemical reactions with which the water-works industry must contend, because water possesses the property of dissolving other substances. In fact, a greater variety of substances is dissolved by water than by any other known solvent.

One of our principal difficulties with iron and steel is that they are highly susceptible to corrosion. Under even ordinary conditions, iron is attacked by oxygen in the presence of water with the resulting formation of rust. Moist air is a corroding agent for almost all materials, except possibly gold, silver and platinum. Structural materials exposed to smoke-laden atmospheres are frequently corroded very rapidly by oxides of sulfur in the smoke. Almost all acids, alkalis and salts used in the water-works industry are highly corrosive. Practically all materials, when exposed to the elements, have a tendency to revert to one or the other of their original forms. Thus, steel corrosion of buried pipes takes a heavy annual toll. Dry-air corrosion may, in some sections of the country, be a very slow process but rare indeed is dry air, especially around a water-works plant! From the standpoint of economy and the quality of the products, we should hurry to recognize the symptoms of corrosion in its early stages and apply treatment at once.

Let us pause for a moment to survey a few water-plant installations that must be protected from the inroads of corrosion:

(1) *Plumbing Lines*—such as steam lines, returns, water and sewer lines, pipe hangers, in fact all steel and, in many cases, cast-iron piping exposed to all conditions. All ground water contains chemicals, such as gypsum, sodium chloride, limestone and sodium bicarbonate, and pipe is often subjected to attack from carbon dioxide and oxygen gases.

(2) *Storage Reservoirs*—which may include all substructural equipment—such as elevated water tanks, hot-water storage tanks, compressed-air tanks and generating sets, compressors, clarifiers, flocculators, filter-bed piping, steel wash-water troughs and electrical conduits.

(3) *Storage Tanks for Acids and Alkalis*—those commonly used in the water-works industry, such as chlorine, sulfuric acid, caustic soda, ammonia, alum, potash and many others.

(4) *The Maintenance of Concrete Installations*—such as sedimentation basins, filter beds, filter troughs and concrete floors, walls and ceilings. These may require a protective coating for the sake of prevention of erosion, waterproofing and appearance.

(5) Last but not least, let us not forget the many metal and concrete exposures in the construction of *dams* that require corrosion protection, such as Tainter gates, drum gates and outlet conduits.

Research in the field of corrosion materials and erosion of concrete has developed many forms of "cure-alls" and preventatives. I am confident, however, that we are all agreed that an effective, cold-applied protective coating would be the most economical solution for the protection of both steel and concrete interiors and is believed to be the best method for protecting surface exteriors.

Naturally, such a protective coating, to be used as a lining, in most cases must be odorless, tasteless and non-toxic, must be impervious to and insoluble in water, most mineral acids, alkalis and salt and must have exceptional abrasion resistance. It must be easily adaptable to field applications, fool-proof as to method of application and economical in cost. Few oil-base paints, if any, can meet such rigid requirements. Thus, the idea of applying a corrosion-resistant, non-water wet plastic material to a surface, the same as one would paint, has aroused the imagination of every engineer who has had the time and the inclination to give it a second thought.

In the development of plastics for protective coatings, not one, but a combination of synthetic, organic plastics is the base substance. There are innumerable chemically resistant resins available but the ones which appear to show the most promise to the water-works industry to date are as follows:

First are the vinyl resins, made by Bakelite Corp. under the name "Vinylite". There are several of these, most of which are copolymers of vinyl chloride and vinyl acetate. One which is believed to have a major use in the water-works field is composed of approximately 87% vinyl chloride and 12% to 13% vinyl acetate. This combination has excellent coating characteristics, making a tough, strong film, which is both water-resistant and resistant to most corrosive chemicals.

The second materials are the Geon resins, made by B. F. Goodrich Co., which are polymers of vinyl chloride or copolymers of vinyl chloride and vinylidine chloride. These materials are also good film-

formers and have excellent water and chemical resistance but are somewhat more difficult to handle than the vinylite resins.

The third are the Saran resins, made by Dow Chemical Co. These are also copolymers of vinylidine chloride and they have considerably more water- and moisture-transmission resistance. These have excellent characteristics.

The fourth is a comparatively new resin, Polyethylene, made by Bakelite Corp. and E. I. duPont de Nemours & Co., which may have some application to the water-works field, since again it has excellent water and chemical resistance. It presents some difficulties, however, since it is not soluble in any solvent at normal temperatures, neither can it be applied as a film in a satisfactory way. It is commonly fabricated as an extruded or calendared sheet or in a similar form.

The fifth is Polystyrene, which is made by a number of companies, the largest of which are Dow and Bakelite. There are some surface coatings that are made from this material but its major use has been in molded objects. It has zero water absorption and extremely fine chemical resistance. As a film former, however, up to the present time, it has been found to be poor because, when precipitated from solvents, it has a tendency to craze.

The sixth are some of the new Silicon resins manufactured by Dow-Corning Corp. They will not water-wet and have a very low moisture-transmission rate. During the war they were used on sensitive radar equipment as a coating to prevent moisture absorption, which could have reduced the efficiency of the electrical apparatus. These resins may at some future date, when the price is reduced, be applicable to the water-works field.

The seventh are Baked Phenolics. These, too, are made by a number of companies, Bakelite being the major. Such surface coatings have excellent water resistance and have been tested for a number of years in boiling water without any apparent effect on the coatings. They have good acid resistance and some of the newer types even have alkali resistance. They would make an excellent coating for steel water pipe, for instance. However, they must be applied in multiple coats and must be baked at temperatures up to 350° F. in order to be effective.

At the present stage of developments then it appears that the most important resins for use in the water-works field are the vinyl types, which include Vinylite, Geon and Saran. Each is extremely resistant to chemical reagents, such as acids and alkalis, and has very low water absorption.

The manufacturers of Vinylite believe it to be probably the most versatile of all plastics and there is much to substantiate their belief. As examples—these resins are used in rigid sheet form for aircraft enclosures, automotive frost shields, slide rules and calculators, plating barrels, luggage and watch crystals. They are used in molding compounds for cosmetic containers, ice-cube trays, transcription records, wire-cable installations and tubing for breweries, hospitals and chemical plants. As an application for surface coatings, these Vinylite resins are extensively used for can linings, pail, drum and tank-car linings, stop-off lacquers for electroplating, linings for washing-machines, waterproofing finishes for tents, raincoats and shower curtains, and concrete swimming-pool finishes.

The Geon resins, also being formulated basically from the vinyl resins, are used for similar conditions. Since they are impervious to oxidation, far superior to rubber in resistance to gas diffusion, waterproof, flexible and tough, Geon resins are used for hospital sheeting, oxygen tents, shower curtains and wearing apparel, such as shoes and foul-weather coatings. Their excellent chemical resistance makes them easily adaptable also as tank linings for corrosive chemicals and as protective coatings for electroplating equipment.

As laboratory curiosities, the materials used in the formulating of vinyl resins have been known for over a hundred years. Yet it is only in the past 15 or 20 years that extensive raw-material sources and economical production methods have allowed the vinyl resins to be produced on a commercial basis.

Carbide and Carbon Chemicals Corp. was first in the United States to manufacture the vinyl materials, which had been discovered by Regnault in 1838. These materials were introduced as Vinylite in 1928. In 1931 the B. F. Goodrich Co. introduced the first non-rigid vinyl-resin plastic. The Monsanto Chemical Co. and E. I. du-Pont entered the field with Carbide and Carbon in 1938 and the Dow Chemical Co. entered in 1940.

It should be pointed out that, while all of these resins have exceptional chemical resistance, there are definite limitations to their use at elevated temperatures. They have been defined as thermoplastic materials, which tend to soften with heat. A protective coating made from a thermoplastic material will not be effective above its softening point, which varies from 140° F. to 200° F., depending upon grade of resin and type of pigmentation.

In formulating surface coatings based on these synthetic resins, they must be cut with suitable solvents, such as ketones and aromatic hydrocarbons, and modified by the addition of pigments, fillers and additional dry resins. The ideal product must have fairly low evaporation rate, so that it can be easily handled. Yet it must dry fast enough so that the object can be readily put into use.

These coatings dry solely by evaporation of the solvents and, when two, three or more coating solutions are applied one over the other, they solidify into a continuous sheet, which actually becomes a plastic protective coating for the surface to which it is applied.

As a further departure from ordinary paint practice, these coatings contain no paint oils, yet form a tightly adhering film over either steel, concrete or wood, without the aid of either heat or pressure.

Synthetic organic plastics as a class have a wide variety of properties depending, of course, upon the substances from which they are derived. For example, could the vinyl resins be used in their native state without the addition of other materials, the coating would be impervious to almost any and all corrosive action, but the resins must be modified to fit them for use as a cold-applied coating and designed for specific requirements. It would be foolhardy to expect a coating that would normally be applied to protect surfaces from atmospheric weathering or chemical fumes, splash and overflow, to be utilized for constant immersion in strong chemicals, over long periods of time. For normal exposure to chemical fumes, splash and overflow, and atmospheric weathering, a different kind of vinyl resin is used from that which would be employed for lining a tank for the transportation of caustic soda, 73% concentration at 230° F.

Let us review a plastic coating system of multiple coats, designed especially as a maintenance coating to withstand chemical fumes, splash, severe atmospheric weathering and continuous exposure to

moisture. Such coatings present a smooth, dense, semi-glossy appearance. They are easy to repair, since the solvents in an added coating penetrate the previous one, to make a continuous unbroken film. They have excellent adhesion, especially where applied over a sandblasted surface, and it is often necessary to cut the base surface before the coating can be removed. They have fine weathering resistance and a very low moisture transfer. Such a system can be used for constant immersion in corrosive waters, whenever surface-preparation specifications include sandblasting. Mineral acid spillage and fumes to which they may be effectively subjected include mild hydrochloric, sulfuric and phosphoric, as well as organic acids, such as citric and lactic, in mild concentrations. The coatings are unaffected by such alkalis as sodium hydroxide and are particularly effective against caustic cleaning agents and sterilizing agents. Manufacturers of these coatings also claim that salts, such as sodium and calcium chloride, sodium sulfate and copper sulfate, have little or no effect on the coatings; also that they have excellent oil resistance and are not affected by ordinary gasoline, Diesel fuel, lubricating oil and similar hydrocarbons, nor by animal or vegetable oils.

Next, let us consider other systems, which also, when applied in multiple coats, may produce a film approximately 0.15 in. thick. These coatings have characteristics of the basic resins ,which are impervious in constant immersion to mild concentrations of acids, alkalis and salts. They have been effectively used for a number of years as linings for tank cars and storage tanks for such products as wines, beverages, lactic acid, mild sulfuric acid and medicinal waters. They are not affected by constant immersion in alkalis, such as 10% ammonium hydroxide and calcium hydroxide, nor in salts, such as 10% ferrous chloride, potassium chloride and trisodium phosphate. These coating systems also have been exposed to constant immersion in distilled water, sea water and tap water for a number of years without any effect whatsoever upon the coating.

The abrasion resistance of these vinyl-base coatings is one of their most outstanding qualities. Hydrostatic tests of a vinyl coating indicate a back-pressure resistance of 10 lb per sq in. Such coatings are employed as linings for all kinds of tanks in the food industry, for the storage of such products as grape juice, milk, olives and tomato

catsup. Millions of square feet of concrete and steel surfaces have been effectively protected with vinyl coatings for the storage of organic materials, such as aviation gasoline, Diesel fuel and ammonia nitrate. Such coating systems are non-conductors of electric current and are highly resistant to electrolysis.

There are other vinyl-base coating systems that have been found adaptable for constant immersion in concentrated mineral acids, most organic acids and caustic soda at 73% concentration, 230° F.

All of these thermoplastic surface coatings have practically no water absorption and very little moisture transfer and are especially tough and non-inflammable. The finished products will not support combustion and will only char under intense heat.

Application may also be made of thermoplastic vinyl-base coatings in lining form. The coating is applied over a sandblasted surface and bonded to the metal by a resin adhesive and the seams are then heat-sealed to form a continuous one-piece lining.

The few years' service record of this plastic, air-dried type of coating in the water-works industry indicates it should have long life. Typical applications lead us to this belief.

First is the Gila and All-American Canals, built by the Bureau of Reclamation, where all the drum gates were coated with a vinyl-type resin-base material in 1940. The Colorado River water has a very high salt content, coupled with extreme weather conditions in the Yuma area. Upon inspection in 1945, the gates were found to be still in excellent condition.

Another is a plastic-coating application on Tiger Creek flume for the Pacific Gas and Electric Co. Here again is a test which indicates the resistance of these coatings to water. The water in the flume has a zero hardness and a tendency to leach the calcium out of the concrete. At the time the test was made, the rocks from the cement were sticking out ¼ in. to ½ in. Applied over a new concrete surface, the plastic coating was in its original condition after four years' service.

Again, on the Grand Coulee Dam, for the Bureau of Reclamation, this type of coating was applied to the steel pier plates, which are the areas at the end of the large drum gates where the steel water-seal operates. These steel plates were coated with a vinyl-base aluminum

coating and are still performing satisfactorily after approximately four years. It may be pointed out that this steel water-seal has been working on the plastic-coating surface every time the drum gate is raised and lowered. As you can readily see, this area would be either fully immersed or in constant contact with water and at the same time would be subject to severe abrasion.

Other applications of which the members of the plastic surface-coating field are justly proud include its application to an electric dredge on the West Coast in June, 1941, for protection against the corrosive action of the sea water. When this dredge was dry-docked in July, 1945, after four years, it was found that, underneath the mussels, barnacles and grass, the plastic coating remained intact and the steel beneath was bright and free from rust, while a similar area, coated at the same time with conventional marine paint, presented a completely etched, corroded area pitted, in some instances, to a depth of 1/16 in.

Steel pontoons were coated more than a year ago and, after severe service up and down the Pacific Coast, the coatings were in excellent condition.

Thus, a graphic picture has been revealed of the protective properties of these vinyl-base plastic coatings which should, with economy, replace the conventional methods of protecting hulls against the corrosive action of sea water.

To review briefly some of the kindred applications in the Middle West and the East, we can point to the application of these thermoplastic coatings to Tainter gates and dam for the Wisconsin Public Service Corp. of Tomahawk, Wis., and to the elevated water tank for the Globe Co., Chicago, Ill., in which case the plastic-base material was applied directly over an oxidized red-lead primer. Still another example is the steel elevated water-tower at the City of Neenah, Wis. Also for the Permutit Co., New York, N. Y., these coatings have been effectively used for lining concrete storage tanks for de-ionized water at several large synthetic-rubber plants.

Exactly how long the thermoplastic resin coatings will last, without additional treatment, obviously has not yet been fully determined. That the life of the coating can be extended by infrequent applications of thin additional coats when necessary is a desirable feature.

The plastic surface-coating field's claims for long life are based upon the fact that the synthetic organic resins are chemically inert and unaffected by aging and the filler materials are equally inert and long-lasting. The solvents used as vehicle leave the coated body upon application and do not depend upon oxidation for drying.

Manufacturers of these surface coatings have so simplified the material that it is neither expensive nor complicated to apply. All of the solutions can be applied with standard paint-spray equipment and most can be applied by brush.

Vinyl resins were among the most critical materials during the war and are credited with contributing much toward winning the war. Now that the "lid is off" as far as priorities of such materials are concerned, the test results made in both field and laboratory and extensive uses in industries with kindred corrosion and contamination problems indicate that there is much to be expected from these coatings for use in water works. Yes, it is apparent that thermoplastic surface coatings usher in a radical departure from old protective-coating methods for steel, concrete and wood surfaces. They now stand ready to combat corrosion problems that in the past have always been a problem in the water-works industry.

Discussion

Roger W. Esty (Danvers, Mass.). How hard a job is it to apply on cast-iron pipe fittings?

Arthur B. Smith. It is not a hard job to apply it. You apply it the same as you would paint. The most important thing to remember about the application of any of these vinyl-base coatings is the surface preparation. Of course that holds true with anything. But we do not beat around the bush and say you can apply it over any kind of a surface. It must be absolutely dry and it must be free of grease and dirt. For cast-iron pipe fittings, for example, I have seen it applied directly. All they did was to use some special cleaner and go ahead with the application the same as you would paint.

Roger W. Esty. How many coats would you suggest?

Arthur B. Smith. Three is the normal recommendation.

Roger W. Esty. How long does it take to dry out?

ARTHUR B. SMITH. That is one of the most outstanding features of these coatings, because they dry by evaporation. They are dry to touch within fifteen minutes. But we usually allow an hour or two to dry between the coats. But a long drying period is desirable, when you are installing in a water district, before you immerse it.

DONALD C. CALDERWOOD (Nashua, N. H.). How expensive is it on the square-foot basis for applying to water tanks?

ARTHUR B. SMITH. On the square-foot basis, the cost of the materials is approximately—for the coating that I would recommend for the inside of a water tank—4 cents a square foot.

DONALD C. CALDERWOOD. That is for the material alone?

ARTHUR B. SMITH. For the material alone. Of course, as far as your application is concerned, it is comparable to ordinary paint in cost of application. You might want to go to a little more pains as far as preparing the surface is concerned.

DONALD C. CALDERWOOD. Is sand-blasting necessary, or is wire-brushing sufficient?

ARTHUR B. SMITH. Sand-blasting is desirable in cases of constant immersion. For exterior surfaces it is not necessary to sand-blast. But where you are putting water inside the tank—where your coating is directly immersed in water—it is preferable to sand-blast.

A MEMBER. Is it best to put this on by brush or by spray?

ARTHUR B. SMITH. The best way is to put it on by spray, with a 360° nozzle, which continuously turns. You pull it through the pipe and the pipe is coated.

ROGER W. ESTY. How many applications in the pipe—three or four?

ARTHUR B. SMITH. Three are preferable.

ROGER W. ESTY. How long do you think they last?

ARTHUR B. SMITH. You have me on the spot there. We really don't have any way of knowing. We know that so far the service has been outstanding; that is, in so far as it has been used extensively in other industries for the past eight years, particularly on the West Coast. It is a subject that we could beat around the bush on a long time. But, as I state in the article, we believe it to be everlasting, because the resins used and the fillers used are known to be everlasting, and the service records that we have on these coatings,

which run anywhere from four to eight years, have proven that they will last that long, at least.

A MEMBER. Under what temperature can it be applied?

ARTHUR B. SMITH. That is a very good question. The temperatures should not exceed 160°, constantly immersed. For instance, in hot water it is not so good, because, being a thermoplastic, it will tend to soften under intense heat. So that, therefore, when you are using it above 160°, it is preferable that you test it first.

A MEMBER. What about the temperature of the surface that you should apply to? Should it be applied to pipe down around 40°?

ARTHUR B. SMITH. Oh, yes, you can apply down to 20° or in some cases even lower. It is being used in refrigerator cars at even lower than 20°.

A MEMBER. How does the coefficient of expansion of the plastic compare with that of steel or copper?

ARTHUR B. SMITH. It will expand very favorably with steel. An example of that is that it is being used by the General American Transportation Corp. for the lining of thousands of tank cars. Outside are some samples that I can show you where you can bend the material all the way around to 180° and back as many times as you want.

A MEMBER. With wide temperature variations, would it expand readily with the steel to which it was applied?

ARTHUR B. SMITH. You mean, in atmospheric conditions?

THE MEMBER. I mean an exposed lining, subject to temperature variations causing the expansion.

ARTHUR B. SMITH. Oh, yes.

THE MEMBER. Would the plastic coating expand with it, or would there be some fracturing of the coating?

ARTHUR B. SMITH. There is absolutely no fracturing of the coating. It will expand or contract, whatever the atmospheric weather conditions may happen to be. As a matter of fact, in one case I know of, it is being applied to a concrete dam by the Commonwealth Edison Co., where the temperature at night may be around zero and in the daytime it may be up around 70° or 80° on this particular project out West.

HAROLD W. GRISWOLD (Hartford, Conn.). Mr. Smith, in the

lining of the pipe by bituminous material, it is often necessary to whitewash the pipe to prevent the sagging of the lining. Is that necessary with plastic coatings?

ARTHUR B. SMITH. No, sir, it is not. The only preparation that is necessary for lining pipe is just to clean the surface as well as you possibly can. In the case of a material that we believe will be the most use to you in the water-works industry, it requires no primer, no body coat, no seal coat. It is a single solution, applied in multiple coats, usually three. Of course, if you have tougher conditions, you would apply another coat. There are some systems which require a prime, body and seal coat, and these three, for constant immersion, have been found to be quite excellent.

A MEMBER. If the pipe is coated and then is stored in the sun, will the lining fall?

ARTHUR B. SMITH. No. As a matter of fact, these coatings are being used for just nothing but pipes which are exposed to atmospheric weather conditions.

THE MEMBER. I mean pipe lined on the inside.

ARTHUR B. SMITH. No, not pipe lined on the inside.

HAROLD W. GRISWOLD. There are some electrical test devices for linings, spun linings, bituminous material, particularly such as is used on the Pacific Coast. I think those tests were high-voltage tests between the brush and the material of the pipe, and they were used to detect pinholes in the lining. Has that sort of test been applied to your material as yet?

ARTHUR B. SMITH. Oh, yes, in a number of cases it has. The vinyl resins are basically porous but we get away from that by using a sealer—that is, in the particular material that I have reference to now. On the prime, body and seal coats, for instance, the prime coat serves as nothing but something to cling to. Then the body coat is composed of a lot of fine silica and vinyl resins—you can see them through the microscope, you can see a thin film on there. Then you have to do something with the surface because of your silica, so that you apply your seal coat, which fills up the pores. There have been any number of tests made of plastic materials for porosity.

One thing I did not mention which might be of some interest to most of you is this: Not so long ago the Army tested 100 different

materials in the country for the lining of potable water tanks and fuel-oil tanks of all descriptions. The vinyl coatings were 1, 2 and 3 on the list and, as a result, specifications were written around the vinyl-type coatings for all of their installations.

ROGER W. ESTY. About how expensive is it?

ARTHUR B. SMITH. In quantity lots on a gallon basis it is approximately $4.00 a gallon. That is for maintenance material. Where you have exposure to mineral acids, salts and that sort of thing—constantly immersed, that is—the expense may be about $5.50 or $6.00 a gallon. But they are all designed for specific purposes. We do not say that the maintenance coating is adaptable for the lining of anything except water tanks. It is all right for that.

A MEMBER. Do these coatings have to be put on by special agents or can the ordinary water-works operator have them applied?

ARTHUR B. SMITH. Anybody who can use a spray gun or a brush can put them on. They do not require anything special in any way whatsoever.

A MEMBER. If this dries in fifteen minutes, aren't you going to get a loss by evaporation in the can itself, and won't you soon have to add a vehicle to it when you open the can?

ARTHUR B. SMITH. No, you don't have to add anything to it. Of course, in the case of any material, if you leave the top of the can off for a long time, some of these solvents will evaporate. In that case, the only thing you do is to add some additional solvent, which is always available. That is the same material that is in there originally. Then you would never use over a pint of solvent to a gallon. It may be sort of a phenomenon, because of the fact that it is not harmed by evaporation. You would think that, if you had a bucket open here for three or four hours, all the solvents would be gone, but that is not true. You may never have to use any solvent. As a matter of fact, we hope you never do, because it reduces the film thickness that you are applying.

WATER-SUPPLY PRACTICE IN GERMANY—1945

BY ARTHUR E. GORMAN*

[*Read February 28, 1946.*]

As a member of a civilian team of technical investigators, organized to serve under the Combined Intelligence Sub-Committee G-2 of the Army and to report on new developments in German utility practices, the writer had an unusual opportunity to observe water utility systems in that country immediately in the wake of World War No. 2. The purpose of this paper is to record some of these observations which may be of special interest to American water works operators.

The period of investigations in Germany was fourteen weeks starting June 1, 1945. The targets visited included 14 public water systems and four large war production plants. The latter included two munitions plants, one chemical plant and one synthetic rubber plant. Conferences were also held with consulting engineers, government officials, plant operators and equipment manufacturers.

War Maintenance and Operation

Considering the extreme conditions under which German water utility systems were compelled to operate during the war, my general impression was that the technical design and operation of these systems were good. As might be expected, the newer developments and the best equipment were observed in plants serving German war production. Apparently these plants were given relatively high priorities with which to obtain material and manpower. As in this country during the war, public utility construction was definitely limited to assure war production. However, there was evidence that operators of these systems were supported by allotment of material and equipment for maintenance and emergency facilities, including those built for protection of major units against bombing and for purposes of camouflage.

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Vulnerability of Utilities

German water and power utilities were vulnerable to destruction by bombing. In many cases water from the various sources is brought to a central well adjacent to a low-lift pumping station. The housing over these structures could readily be detected from the air. In effect, they are on the jugular vein of the system. Their destruction would result in immediate interruption of supply to that system. Strangely, in spite of their vulnerability, selective bombing of central collecting wells and pumping stations in German water plants was not carried out by either the American or British air forces.

The destruction observed in German water systems was especially heavy in the transmission and distribution systems. Much of this destruction occurred in the late months of the war, when aerial bombing was most intensive. German water works operators expressed surprise that allied air forces followed a policy of intensive bombing of war production plants, when periodic destruction of water works intakes or pumping stations would have effectively stopped production at these plants. Such major war-production items as synthetic gasoline, rubber, chemicals and munitions require heat-exchange units which use large volumes of water. An interruption of supply would necessitate a shut-down of operations.

Attempts to Camouflage Systems

Realizing the vulnerability of water supply and pumping units at such plants, the Germans resorted to various methods of deception. One which was quite successful at two munitions plants was to house the water pumping and treatment facilities in separate buildings, which resembled typical German farm houses. Such plants were frequently built in wooded areas. If the utility buildings were exposed, they were so grouped and served by access roads as to resemble rural houses with their typical stone or stucco exteriors and red tiled roofs. In one acid-recovery plant in a heavily wooded area, a steel stack was painted green and was equipped with a telescope device, which would permit lowering to tree height when bombers approached. Buildings were half underground and half above ground, with flat-slab roofs covered with top soil in which grass, shrubbery and small

trees were planted for camouflage. Edges of the roof were saw-tooth, to cast shadows similar to those of the surrounding fir trees. These plants were operated partly by slave labor and, in the days following liberation, the freed laborers destroyed much operating equipment and many records. At the Bremen water works, camouflage of the open settling basins and slow sand filters apparently attracted the attention of our air reconnaissance officers, because this plant was heavily damaged by aerial bombing. At the time of inspection—July, 1945—one of the two settling basins, eleven of twenty-two slow sand filters and one of two filtered-water storage reservoirs were out of service for repairs. Had it not been that about one-half of the water supply of Bremen is obtained through a large gravity transmission main from an impounded supply in the Harz Mountains, this city would have been almost entirely out of water for a long period. As discussed later in this paper, water service in that city suffered heavily, both from American and British bombing and also as a result of demolition by German army engineers.

Sources of Supply

In considering German water works operation in comparison with American practice, one must consider that the per-capita use of water in that country is low. It varies in the larger cities from 40 to 60 gal per day or about one-third the normal use in our cities. About 75% of German public water supplies are from ground sources. These include deep and shallow wells, springs and infiltration galleries. Surface water is stored in open reservoirs typical of those used to supply water to large cities in New England. River supplies in Germany are filtered, either naturally by percolation through sand and gravel substrata to infiltration galleries or artificially in slow or rapid sand filters—in the latter case usually without chemical treatment.

Wells

Much of Germany is underlain with an almost inexhaustible supply of cool, clear ground water. The drain of war production on underground well supplies in that country was not serious, as was the case in many local areas in the United States. The shallow type of wells predominates. Usually they are hand- or machine-dug, 40 to 60 ft in depth. They are lined with stone, brick and pre-cast

concrete. Before the war, well screens of copper alloy were most common. Since the war, because of the shortage of copper, screens have been made of steel covered with rubber, of fluted glazed ceramic material and of oak wood. Spacing of wells varies widely depending on local conditions. The more frequent spacing ranges from 60 to 120 ft. At the head of each well is a valve box of brick or concrete with locked cover, flush with or just above the surface of the ground. Wells are connected by a cast-iron header system leading to a central collecting well, from which the water is pumped for treatment. The header system is usually under negative pressure maintained by a vacuum pump, the head depending on the rate of withdrawal desired. Deep wells vary in depth from 300 to 1500 ft. Usually they are operated as separate units. Deep-well pumps observed were of the series-impeller and submerged-pump-and-motor types.

In Germany ground waters often contain objectionable amounts of carbon dioxide, iron and manganese in solution and, therefore, must be treated.

Carbon dioxide is removed by passing the water in part or whole through tanks containing milk of lime. The Bücher process, in which hydrated lime is added to the reaction tank in proportion to the flow of the water to be treated, was used in most of the plants visited. The precipitated calcium carbonate is discharged intermittently from the settling cone to the sewer. Treatment to reduce carbon dioxide has been carried out in Germany since it was shown that the Leipzig lead-poisoning outbreak was the result of action of water high in carbon dioxide on lead in service pipes. In this outbreak there were 50 severe and 200 mild cases of lead poisoning.

Soluble iron (2.0 — 0.5 ppm) is removed to 0.05 ppm by aeration, settling and filtration. The water is pumped to various types of distributors, from which it trickles down over staggered brick aerators about seven feet high and is then collected in settling basins, either under or adjacent to the aerators. At intervals of about six years, the bricks are cleaned; the oxidized iron is removed by air drying and wire brushing. With one to two hours' retention after aeration, 75% of the iron is removed before filtration. Filters are of rapid

and slow, gravity and pressure types, using sand as the filter media. Rates of filtration are in line with American practice.

Manganese (1.0 ppm and higher) is removed from German waters by filtration in gravity or pressure filters in which the filter medium is a calcined dolomite. It resembles crushed pottery clay, is very porous and consists of calcium and magnesium oxides and carbonates. The medium must be replaced about every six to eight years.

Infiltration Galleries

In Germany infiltration galleries are commonly used for the collection of water for public systems. They are of three types: (1) galleries adjacent to rivers or artificial recharge areas; (2) galleries cut into the sides of hills or mountains to intercept the flow of water through seams in rock, and (3) galleries in artificially built collecting areas between hills.

At Essen in the lower Ruhr Valley, the infiltration galleries are parallel to the river and about 30 ft deep. The pipes are of steel and reinforced concrete and are perforated or slotted to collect the water which infiltrates into the sand and gravel in which they are set. Part of the water reaches the galleries by natural infiltration from the river. To supplement this, long narrow basins of reinforced concrete have been built in the low area back from the river, which has settled because of coal removal from below. These open-bottom basins are filled with 4 to 6 ft of sand and are flooded by direct flow from the river. In effect, they are slow sand filters built over or adjacent to the galleries. When the filters are clogged they are raked and the dirty sand is piled and removed. Replacement of filter sand is necessary at about 8-year intervals. Because of proximity to the Ruhr River, the area at Stelle where the filters and galleries are located, from which water is supplied to the city of Essen and vicinity, had been heavily mined by the German engineers. Several water works employees at work in the filter area had been killed by explosions of these mines.

At Hagen in the Upper Ruhr, a modern rapid sand filter plant was constructed to permit increased output from the infiltration galleries. By applying filtered water to the slow sand filters they

were able to recharge the galleries at high rates and with less manpower. Prior to the construction of the rapid sand filter, difficulty had been experienced in getting enough water to the galleries by natural percolation from the river or through the slow sand filters, during periods when algae were prolific in the river water. The temperature of the water in the infiltration galleries along the Ruhr fluctuates seasonally, being slightly less than that in the river.

The system of infiltration galleries which supplies water for the city of Munich is most interesting. About 20 miles south of the city, in the foothills of the Bavarian Alps the city has developed a series of infiltration galleries in the Mangfall Valley. The collecting galleries are semi-elliptical in section and are about 3 ft wide by 5 ft high. They are constructed of open-jointed stone and brick and also of concrete with slots in the sides and top, through which the ground water can enter the galleries. Some of the galleries are in the river valley and others are cut into the rock of the hills to intercept the underground flow. The water is clear and has a temperature the year round between 40° and 50° F. In one case, the water from a series of radial galleries is discharged into a central collecting well, lined with white tile. Flow to the terminal storage reservoirs near the city is by gravity, through steel and reinforced concrete transmission mains, and is measured and controlled at a Venturi chamber near the head works.

At the Ranna works supplying about one-half the water to Nürnberg, a novel infiltration gallery has recently been built. A swamp caused by outcrop water between two hills about 30 miles northeast of the city was excavated to a depth of 25 ft, back-filled with gravel and covered by a concrete slab. In the gravel two 30-inch collecting pipes were placed, which deliver the intercepted water to a storage reservoir and control works. Over the concrete slab sand and black dirt were placed and plantings were made to conceal the collecting gallery. A supplemental supply was obtained from an infiltration tunnel, similar to those of Munich, extending 1500 ft into a mountain to intercept an underground flow of water discovered by exploration.

The quality of the water from the Munich and Nürnberg infiltration systems is good and no further treatment, except chlorina-

tion in the terminal reservoirs, is necessary. The advantage of having a source of supply producing a clear and uniformly cool water, free of algae, is obvious. Unfortunately time did not permit a study of the economics of the Munich and Nürnberg systems of infiltration galleries, on which comparisons as to cost with other systems of surface storage could be made. The higher per-capita use of water in the United States might make the cost of developing infiltration galleries too expensive for acceptance here. Nevertheless, this aspect of German water-supply engineering was most interesting and is worthy of further study.

Surface Supplies

Storage of surface water collected from sparsely settled and wooded areas, as is practiced by New York and Boston, is also carried out in Germany but, before such water is supplied to consumers, it is filtered. Examples of surface storage were the reservoirs of the Harz Mountain Water District, organized by the Province of Hanover to supply water to a score or more of cities and villages between Osterode and Bremen and, on the east side of the province, to Brunswick and many other villages along the route of the transmission main. The two dams are known as the Sösetalsperre and the Eckertalsperre. A private water company known as Wasserwerke Landkreiss Aachen has two impounding reservoirs in the hilly wooded area southeast of Aachen. From these reservoirs water is supplied mostly by gravity to the coal mines and industrial area of 750 square miles east and north of that city. Through an elaborate system of pipes and storage reservoirs, water is supplied to more than forty villages and towns, including such cities as Stolberg, Eschweiler, Elendorf and part of Aachen, and is even transmitted across the border into Holland. The Haspetalsperre dam and reservoir on the Ruhr, above the city of Hagen, furnish another example of storage of surface water for public water supply as well as for control of the flow of that river for sanitary and power purposes.

The dams across the valleys to permit development of these reservoirs are of concrete and stone construction and were well maintained. Because of the serious destruction to the Möhne dam on the upper Ruhr by the British air raid of May 17, 1943, the Ger-

mans had lowered the water level in all large storage reservoirs. At the time of our visit there was some concern that a deficiency in rainfall would cause a serious shortage of supply. The Möhne dam had been repaired but the destruction in the valley below, caused by the onrush of water released through the breach in the dam, was clearly evident. At the Hagen filtration plant, below the Hengstey See and about 30 miles downstream from the Möhne dam, the flood-water mark could be seen on the side of the building, about five feet above ground level.

Water Treatment

Rapid Sand Filters

German rapid sand filter plants of the gravity type were visited at Hagen, Wulzdorf near Bremerhaven, Osterode and Stuttgart and at large war production plants at Schkopau, Leuna and Helsa. With the exception of the one at Osterode, these plants had been built within the past decade. They were well designed and were equipped with modern control facilities. The most interesting features were the absence of overhead wash-water troughs, the design of the filter bottoms and strainer systems and the use of air and water for backwashing.

In Germany, manufacturers design and build water works structures and facilities. The two most important types of rapid sand filters are known as the WABAG and the BAMAG types. Filter plants are constructed with either central or side galleries (see Figure 1). The filters are two to three times as long as they are wide, the narrow side being parallel to the gallery. Raw water enters a long inlet channel on one side of each filter. When washing, this channel also serves as an outlet channel, discharging to a sewer in the gallery or at the far side of the filter from the gallery. Between pairs of filters there is also a common deep wash-water channel. Since filters are about eight feet wide, the travel of wash water from the center of a filter to the wash-water channel is not over four feet.

The WABAG filter bottom, shown in Figure 2, is made up of a series of pre-cast reinforced concrete slabs, about 6 in. thick, 18 in. wide and 36 in. long. Into threaded holes in the slab, spaced about 3¾ in. on centers, special copper or glazed porcelain strainer heads

FIG. 1.—FILTER GALLERY AT BUNA-WERKE WAR PRODUCTION PLANT, SCHKOPAU, GERMANY.

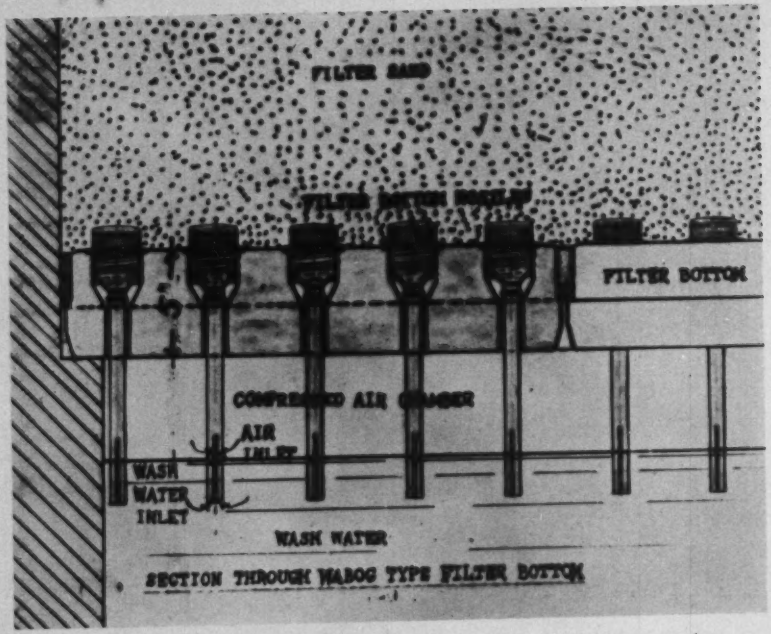

FIG. 2.—SECTION THROUGH WABAG-TYPE FILTER BOTTOM, SHOWING NOZZLES FOR AIR AND WATER WASH.

are screwed. Each strainer has an extension nipple protruding into the space below the slab, a distance of about six inches. When a filter is to be washed, compressed air is pumped into the space under the slab and enters the filter through the strainer extension pipe and head. Water is then pumped into the space below the slab and the filter is back-washed with a mixture of air and water. The air which is compressed in the upper part of the space under the slab enters the strainer extension pipe through a slot or holes in the side. Finally, to free the filter of entrained air, it is washed with water only. This type of filter has no gravel bed, the sand being placed directly over the strainers. The depth of sand is about 6 ft. The sand size varies from 1.0 to 0.6 mm. Such filters were being used with and without pre-treatment. At the Buna-Werke at Schkopau, where Salle River water was treated, the settling time was only one hour and no chemicals were used for coagulation. At other plants chemicals were used only when the water was turbid. Often there was no provision for pre-settling. Operators reported freedom from mud-ball difficulties and were well satisfied with results obtained from these filters.

The BAMAG filters, while similar to the WABAG plants in general layout and arrangement of inlet and wash-water channels, use a pipe manifold with porcelain nozzles for wash water. The distributor pipes are placed on coarse gravel, about one foot from the filter-box floor. The pipe grid for the air wash is set in finer gravel, about 10 in. above the wash-water distributors and midway between them. The sand depth above the gravel is about four feet. Its size is similar to that in the WABAG filters. Design rates for both filters are in line with American practice.

Rapid sand filters of the steel-tub type with mechanical rakes were seen at Charlottenburg, a suburb of Berlin.

Slow Sand Filters

Slow sand filters were seen at Bremen and Halle, as well as at the Probstheide and Thekla plants in Leipzig and the Tegel and Müggelsee plants in Berlin. Except at Bremen, the filters were covered and were operated to remove iron from ground water after aeration and settling. The filters at Bremen were open and treated Weser River water after 24 hours' settling—normally without chemical treatment.

I was surprised at the number of new steel pressure filters seen in Germany, especially in view of the reported shortage of steel during the war. They were used for iron and manganese removal, as well as for roughing filters in lieu of settling, where production from rapid sand filters was restricted when algae were numerous in raw water supplies. Pressure filters were common in war production plants. They were single-, double- and triple-decked and ranged in diameter from about three to six feet.

Chemical Handling and Mixing

With the exception of that collected from infiltration galleries, most of the water supplied in the German cities visited was filtered. In general, operation and maintenance of these plants were good. The use of coagulants was the exception rather than the rule. Several plants which normally do not coagulate the water prior to filtration use aluminum sulphate when the raw water is highly turbid. Only one plant used any other coagulant. This was at a munitions plant in Ebenhausen, where Parr River water used for industrial purposes was coagulated with ferric chloride. At the same plant, well water for domestic use was treated with aluminum sulphate.

Chemical handling, storage, mixing, measuring and conveying practices in Germany are similar to those in the United States. Handling in bulk is more by manual labor than by mechanical equipment. Cranes and conveyors were seen but no vacuum systems were observed. Batch mixing is common. Mechanical stirring is general. Measurement is both gravimetric and volumetric. Rotameters are used in many plants. Duplicate equipment is not unusual. Rates of application in proportion to flow are controlled both automatically and manually.

Solution tanks are of steel, concrete and wood, with linings of hard and soft rubber, porcelain and wood. Chemical piping is made of lead, bakelite, plastics, hard rubber and steel with rubber or porcelain linings. Chemical feed pumps are lined with bakelite and plastic. At the Osterode plant in the Harz Mountains, the chemical solution was filtered before being pumped to control devices.

Slow mixing (10-20 minutes) by vertical mechanical stirrers is used in the BAMAG-type rapid sand filter plant at the Hagen Hengstey

See plant. Mixing is accomplished at the Hagen Haspetalsperre plant, of the WABAG type, by the hydraulic-jump principle. Around-the-end mixers are used at the Osterode plant.

Softening

The waters in German plants visited varied in hardness from 10-20 ppm in the surface water to 500 ppm in well and river water at Stuttgart. The range of hardness for most of the shallow well waters was between 100 and 200 ppm. No treatment plants for softening were seen, except those for boiler feed-water and special processing at industrial plants, where zeolite softeners were used.

Chlorination

German water works operators do not give the attention to chlorination that is considered good practice in the United States. Ground waters are of good quality and do not require much chlorine. Usually from 0.1 to 0.2 ppm of chlorine is applied to the water entering filtered-water reservoirs. Residual chlorine is rarely found in distribution systems. Except at Stuttgart, where super-chlorination and de-chlorination are practiced, the largest amount of chlorine applied to filtered water was 0.6 ppm at the Tegel plant in Berlin. It is customary at this plant to use ammonium sulphate with the chlorine to form chloramines. The ratio of chlorine to ammonia used was 2 : 1. An effort was made to carry about 0.4 ppm of residual chloramine in the reservoir from which water is pumped to the system.

Chlorination equipment is not as well housed or maintained as in the United States. Separate rooms for the chlorine and the chlorine control equipment were rare. Use of chlorine in large-capacity containers, equivalent to the ton containers so common in the United States, was observed at only two plants. Periodic weighing of cylinders, to check the operation of chlorine control equipment, was reported at only one or two plants. Hourly records of chlorine applied and residual tests are not customary. Duplicate chlorinating units were observed at several plants. Automatically controlled chlorinators were seen at one plant in Berlin and one at Osterode. The use of rotameters to measure the flow of chlorine gas was observed at several plants.

The Stuttgart water works had the most interesting chlorination plant seen by members of our party in Germany. Here super-chlorination (5.0 to 9.0 ppm) is followed by de-chlorination through granular activated-carbon filters. De-chlorination was being practiced at only one other plant—in the drinking water system at the Buna-Werke at Schkopau, where the water was de-chlorinated by passing it through a granular carbon pressure filter.

Water Quality

The quality of German water supplies as delivered to the consumer is generally good, although in many cities water is quite hard. Free carbon dioxide in well waters often ranges from 40 to 60 ppm. It is removed or reduced by treatment with milk of lime, as previously described. Iron is common in well waters, ranging from 0.5 to 2.0 ppm. It is removed to less than 0.05 ppm and often to 0.02 or 0.01 ppm. Manganese in well water may be as high as 1.0 ppm and is almost entirely removed by treatment. The hardness of German water is largely temporary or carbonate hardness, although there are exceptions where sulphate hardness is high. Public water supplies vary in degrees of hardness from 10 to 500 ppm, the more common range being from 100 to 200 ppm. German water supplies investigated had a pH range of 7.2 to 6.5.

Micro-organisms of the types experienced in the United States are common in surface waters in Germany. Their growth is watched carefully and plant treatments are adjusted accordingly. At no city was the use of algicides reported. Copper and copper compounds are expensive in Germany and were not readily available during the past decade. Biologic pollution of German water supplies at the source is not heavy, except where river water is used. Even without chlorination, the water produced at most plants after filtration is bacteriologically of good quality. In the plants of the larger cities, chemical and bacteriological laboratories are maintained and the technical control over the treatment is good. Public health officials also collect and analyze samples from the plants and the distribution systems.

Transmission Mains

German transmission mains are constructed of steel, cast iron, reinforced concrete and, in the case of gravity lines, pre-cast and cast-in-place concrete and three-ring brick. Sizes vary from about 12 to 72 inches in effective diameter. Most German cities have multiple sources of supply and therefore many transmission mains. This gives wide flexibility in operation—an especially desirable condition under war conditions. But in spite of this, destruction of transmission mains by aerial bombing was heavy. At Leipzig, the Carnitz and Thallwitz plants in the Russian zone of occupation and the Naunhof plants in the American area could not supply the city, because of damage to transmission lines by bombs dropped by American airmen just prior to occupation late in April. Fortunately, the reservoirs at the Probstheide plant in the city were full prior to the bombing. By rationing of water and use of supplemental supplies pumped in from suburban systems and emergency wells constructed at numerous points in the city, complete failure of water service was avoided. In addition to damage to the water transmission mains at Leipzig, bombs damaged the main pressure sewer to the broad-irrigation sewage farms in the suburbs and for many weeks it was necessary to discharge raw sewage to the Elster River.

In Bremen destruction of transmission mains was especially serious. The water filtration plant is in Neustadt across the Weser River from the main city. The five cast-iron and steel transmission mains crossed the river on three bridges. In addition, one large steel transmission main was laid under the river. As a result of American bombing, two of the bridge lines and the one under the river were broken and rendered useless. In demolishing the bridges the German engineers destroyed the other three mains, leaving the city without water, until American military engineers suspended steel mains across the demolished bridge spans.

So intensive was the bombing in Nürnberg that all but one of six transmission mains were out of service when the American Army entered the city about the middle of May.

Storage Reservoirs

Water storage reservoirs in Germany are usually covered and well concealed. They are of brick and concrete and are built in multiple units. The newer ones at Munich, Nürnberg and Kassel were most interesting and in appearance surpassed any I have seen in the United States. The Kreupullach Reservoir at Munich, of 262 mil gal capacity, built in 1937, was exceedingly attractive. In the white-tiled control room there was an electrically illuminated wall diagram, which showed by colored lights what valves were open, the elevation of water in each unit and the flow in and out of the reservoir. The interior finish of the reservoir was white. Ventilation was good and condensation at a minimum. An inspection gallery lined in white tile crossed the reservoir. Lights with white reflectors were numerous and, when they were turned on, the deep-blue color effect of the water was striking. Valves, gates, doors and operation mechanisms were of polished non-rusting steel. What a contrast they presented to the dark, damp, inaccessible, rust-streaked, poorly ventilated reservoirs so common in this country!

Drainage from this reservoir was not wasted to the nearby stream but was discharged to a concrete basin in the valley, from which the water was discharged to wells to recharge the underground supply. Floating islands of logs, covered with top soil and small bushes, served to camouflage the open receiving basin by minimizing the surface area of the water. The underground Venturi- and valve-control chambers were also well camouflaged. They had ground-level access doors which, when unlocked, opened automatically because of counterweights. Visitors were not permitted to enter the Schumhausenbuch Reservoir at Nürnberg, unless they wore felt shoes over their regular ones. A bomb dropped on the roof of this reservoir sheared a hole 50 ft in diameter through the roof.

Elevated Tanks

Elevated steel tanks enclosed in stone and brick towers are common in Germany. Many are artistically designed. Booster pumping stations at the street floor, with quarters for housing employees or for supply storage on upper floors, are not uncommon. Many were seriously damaged by bombing.

Pumping Equipment

In German water works steam- and electric-driven pumping units of many types are used. In low-lift pumping plants visited, more old steam crank-and-fly-wheel and triple-expansion pumping engines were used than is customary in the United States. High-pressure pumping equipment is of much more modern design. Motor- and steam-turbine-driven centrifugal pumps are common. The newer stations are well laid out and are equipped with modern control and recording equipment. In Berlin, standby Diesel engine generators were used at one of the large electric stations. Both hard coal and brown coal briquettes were used for fuel. Much more hand-firing of boilers was observed in the steam plants than in America. The larger stations were equipped with stokers. Stacks at power plants were not damaged by bombing unless there was a direct hit.

Heavily reinforced concrete shells in inverted U and V shapes were set over pumps and motors, in order to protect them against falling debris in case of bombing. Single and double heavily reinforced concrete housings, cylindrical and rectangular in shape, with steel doors, were built in the operating rooms of water treatment and pumping plants to protect employees on duty. Special outside or underground air-raid shelters or "bunkers" were built for the protection of other plant employees during periods of bombing.

Distribution System

The distribution systems of German water works are about 90% iron. During the war, steel was used to considerable extent for repairs. The sizes vary from about 3⅛ to 39 inches in diameter. The most common sizes range from 4 to 10 inches. Pressures in the system vary from 25 to 70 lb per sq in. Damage to the distribution systems was extensive and temporary service through fire hose and rapid-joint steel pipe, laid on the surface, was resorted to after air raids.

At Essen, where aerial bombing was heavy, 2.0% of the entire water distribution system was destroyed by bombing. Many sections of bombed cities were out of water for weeks. Frankly, after seeing the extent of damage to water mains and sewers in German cities and

realizing how little residual chlorine was being carried in the water in the distribution systems, it was a surprise to me that waterborne epidemics had not occurred in most large cities. Water was transported in tank wagons and consumers were required to carry water in pails from temporary supply stations.

Cast-iron pipe fractured easily in the area affected by bombs but breaks usually stopped at joints. German utilities carried large stocks of cast-iron and steel pipe for emergency repairs. A special mechanical joint with rubber gasket permitted quick replacement of damaged cast-iron pipe. This pipe is very popular with German water works engineers and has much to commend it to American engineers. Steel pipe was crumpled, twisted and ruptured by the impact of bombing. At Munich it was reported that, even after repairs had been made to steel pipe, leaks were found at various distances back from the bomb crater which required subsequent excavation for pipe repair or replacement. Apparently, with a direct hit by a bomb, a shock wave transmitted by the water created stresses which ruptured the pipe some distance from the point of impact.

Some idea of the damage which bombing caused to German water distribution systems may be obtained from the following:

War Damage to German Water Distribution Systems

City	Pipe in system (kilometers)	Breaks in system
Essen	1,000	2,000
Munich	1,700	1,860
Bremen	1,200	1,200
Nürnberg	670	1,200
Halle	362	200
Hagen	60	200

Hydrants and Valves

The most common fire hydrant used in Germany is the underground type. Access to the outlet and control valve is made possible by removing a cast-iron cover, set in a frame flush with the pavement. An extension pipe, 2½ in. to 4 in. in diameter, with a bayonet-type fitting is slipped over the outlet and by twisting it is held firmly in

place. To allow flow to the hydrant, the valve is opened by a long key. Fire-hose connections are made to the extension pipe, which protrudes about 3 ft above ground. When service is no longer needed, the valve is closed and the extension pipe is removed. In cold climates these hydrants are difficult to maintain, because of freezing of the cover in place.

German fire department officials prefer the above-ground hydrants which are similar to American hydrants. It was observed that the above-ground hydrants were numerous at all large German war plants. They were used around such new buildings as the I. G. Farben office building in Frankfurt, which was occupied by SHAEF and later by the ETUSA. These hydrants were also seen in the high-value property areas of large cities. German water works engineers expressed the opinion that these above-ground hydrants would eventually replace the underground hydrants in large cities, even though their cost is two to three times that of the older hydrant.

Valves in German water systems are well made and are similar to American manufacture.

The location of both valves and hydrants is well identified in Germany by signs posted on the walls of nearby buildings. Enameled signs similar to automobile plates show by letters, arrows and numbers the exact location of underground operating facilities and the size of the main they serve. At plants where multiple water systems are used, signs of various colors and borders serve to identify the different systems. Manhole covers are also identified by special markings in the castings.

Service Pipes and Meters

Service pipes in Germany are of lead and galvanized iron. Copper is too rare for such use. All services are metered. Disc- and sleeve-type meters are common on domestic services. In-line rotary meters are used on larger ones. Plastic and pressed-fibre discs, rotors and gears are used in German water meters.

SUMMARY

In conclusion, the following is a general summary of observations as to German water-works practice in 1945, as recorded above:

1. Considering war conditions, German water utilities were well maintained and operated.

2. German public and industrial water utilities were vulnerable but, in general, they were not made special targets in American and British bombing attacks.

3. Destruction of German transmission and distribution piping by aerial bombing was very heavy, especially in the later months of the war.

4. German water works designers and operators gave special attention to camouflaging plants and to protecting vital equipment and operating personnel against aerial bombing.

5. About 75% of German public water-works systems depend on ground water for their source of supply.

6. Treatment for removal of carbon dioxide, iron and manganese is common in Germany.

7. The Germans use various types of infiltration galleries to obtain water for public supplies. The design and economics of these systems are worthy of study.

8. The design of German rapid sand filter plants, especially in the use of air and water for filter washing and the design of inlet and wash-water channels and filter-underdrain systems, is most interesting.

9. Chlorination practice in Germany is not up to American standards.

10. Some of the newer storage reservoirs seen in Germany were superior in design and equipment to American structures of this type.

11. In the large cities in Germany, pumping equipment compares favorably with American standards. A considerable quantity of old steam pumping equipment was being used.

12. Distribution mains were seriously damaged by bombing. A special mechanical-type cast-iron pipe joint was very effective in making emergency repairs.

13. While underground fire hydrants prevail in Germany, the trend is toward above-ground hydrants.

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While the writer served as a member of the War Utilities Sub-Committee, Technical Industrial Intelligence Committee, C. I. O. S. G-2, U. S. Army, in making many of these surveys, he was accompanied and assisted by Drs. Anthony J. Fischer and Arthur V. Sheridan of the Safety and Technical Sub-Committee. Later the T. I. I. C. team was supplemented by Lt. Col. Joseph J. Gilbert, Sn. C., representing C. I. O. S. and the Surgeon General's Office, U. S. Army, and he was assisted by Major Myron W. Tatlock and Lt. Harold P. Pfreimer, both affiliated with the Allied Military Government in Germany.

MATHEMATICS AS A TOOL IN THE WATER-WORKS LABORATORY

BY HAROLD A. THOMAS, JR.*

[*Read at Chemists' Round Table, February 28, 1946.*]

The Statistical Approach. Statistical methods are especially adapted to the analysis of quantitative data affected by many causes. The analytical data determined in the water-works laboratory can best be analyzed by the *statistical method.* This method deals with a series of observations of a kind that in general vary with time and which, in addition, cannot be made with complete precision, because of (1) fluctuations inherent in all sampling procedures, or (2) imperfections in laboratory technique and method. The statistical approach may be illustrated at the hand of an example as follows:

Example 1. Color (ppm) in raw water, Biddeford, Me., water supply, 1939:

Month	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
Color, ppm	51	39	53	55	48	41	37	56	30	31	55	46

Ave. color = 45 ppm.

Analysis is facilitated by arrangement of the data in order of magnitude:

30	31	37	39	41	46	48	51	53	55	55	56

From this statistical array the *cumulative frequency distribution* may be drawn. The first item, 30, represents 100 ÷ 12 = 8.33% of the total number of months and hence is plotted at the point, 8.33% and 30, on the graph (Fig. 1). Results for successive months are plotted in order of magnitude, each at an ordinate 8.33% higher than the preceding, until the steps reach the 100% line as in Figure 1.

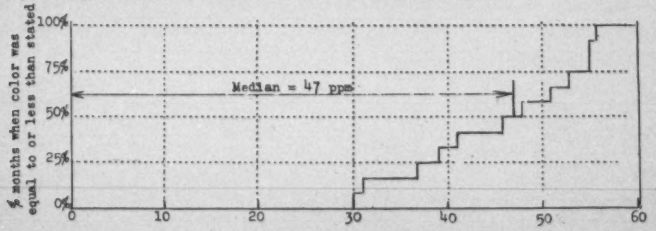

FIG. 1.

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A cumulative frequency distribution reveals the essential statistical characteristics of a series. In general, two important properties of distribution are manifest. These are (I) a tendency of most of the items to be grouped in a central zone and (II) a dispersion of the remaining items at various distances from the central cluster—the smaller the dispersion, the steeper the steps in the diagram. Both of these properties must be adequately described in order to provide a satisfactory description of the series. The *first* property, that of defining the general location of the curve, is commonly given by two kinds of averages, the *arithmetic mean* and the *median*. Both of these quantities are represented on the cumulative frequency diagram.

The arithmetic mean is proportional to the area over and to the left of the step diagram. In the example, this area is 4,500, and the mean is 45 ppm.

The Median. The median is that point where the curve crosses the 50% line. As may be seen from the diagram, the median value of the foregoing series is 47 ppm.

In many respects the median is a more useful measure of central tendency than the arithmetic mean. It is easily computed and is less affected by erratic, extreme items. The arithmetic mean, on the other hand, is greatly affected by extreme values and for some purposes renders a distorted, atypical representation of the data.

Dispersion. The *second* property of the series, the dispersion, is measured by a number of quantities, the most useful of which are the *variance* and the *standard deviation.* The variance is the sum of the squares of the deviations of the items from the arithmetic mean, divided by the number of items. The variance, s^2, of the foregoing example, computed in accordance with this rule, is as follows:

$$s^2 = \frac{1}{12}\left[(30-45)^2+(31-45)^2+\ldots+(56-45)^2\right] = 80.6.$$

The standard deviation, s, is the square root of the variance. It has the advantage of being measured in the same units as the items of the series and also the mean. In the example,

$s = 9$ ppm.

The *coefficient of variation* is defined as the standard deviation divided by the mean. In the example,

$s/M = 9/45 = 0.20$, or 20%.

The mean and the standard deviation of a series provide a much more complete description of a series than is afforded by the mean alone. In rapid sand filter plants wherein color in raw water determines coagulant dosage, and hence chemical costs, the mean color during a year (say) cannot be correlated perfectly with chemical costs. The mean color for two successive years at a plant may be nearly the same, but amounts of chemical used to obtain requisite purification may differ significantly during the two periods, if the standard deviations of color distribution are not the same. It is not only the overall average of color intensity but also the variation in color that determines operating costs.

The following approximate rules are useful in fixing ideas as to the meaning of the standard deviation, as a measure of the non-uniformity of a series:

I. About two-thirds of items (months) in *typical* series fall within an interval, $M - s$ to $M + s$.

II. More than three-fourths of items in *all* series *must* fall within an interval $M - 2s$ to $M + 2s$.

Often in order to provide some notion as to the non-uniformity of a series, the *range*, defined as the maximum minus the minimum item, is stated in water works literature. The range manifestly is an imperfect and often inadequate measure of non-uniformity, because it is based upon only two observations and these represent extremes that are inherently erratic. However, in view of the widespread use of the range in water works literature, it is pertinent to point out the relationship of the range to the standard deviation. This relationship for normal distributions is expressed in the following table:

Number of items in series	Average value of ratio, range to standard deviation
5	2.33
10	3.08
15	3.47
20	3.74

According to this table, the range in the series of the example would be expected to be $9 \times 3.1 = 28$ ppm. The observed range, $56 - 30 = 26$, is in fair agreement with the expected value of 28 ppm.

Error Analysis. The mean and the standard deviation are use-

ful in determining the magnitude and effect of errors inherent in laboratory procedures. When repetitive determinations are made from a single sample, the standard deviation of the resulting series is called the *standard error*. In *precise* measurement the standard error relative to the mean is a small quantity.

Example 2. An experiment may be used to bring out the salient features of the distribution of results in replicative water-works laboratory determinations. The following counts were obtained on 15 plates made from a sample of raw water: 147, 154, 123, 142, 141, 130, 149, 146, 161, 142, 173, 143, 151, 158, 183.

In this series, the mean is 150 bact/ml and the standard deviation 14.7 bact/ml.

Ordinarily, a distribution of plate counts of bacteria may be expected to yield a value of standard deviation about equal to the *square root of the mean*. Thus the expected standard deviation would be $\sqrt{150} = 12.2$ bact/ml. If the *actual* standard error differs considerably from the *expected* value, it may be inferred that laboratory technique is at fault (insufficient shaking or inaccurate apportioning of sample upon plates, etc.). In the example, the actual standard error does not differ significantly from the expected value, and adequate technique may be presumed.

Error of a Mean. If several sets of 15 plates each are tested from the same sample, it is not to be expected that the mean of each set will turn out to be exactly 150 bact/ml. Some variation in means would be expected, but it is intuitively felt that this variation will not be as large as the variation in the items from which the means are calculated. Experience indicates that the reliability of a mean, which is measured by the *standard error of the mean*, bears a direct relation to the standard deviation of the series. This relationship is stated in the following rule:

The *standard error of the mean* of a series is the standard error of the series divided by the square root of the number of items—

$$s_M = \frac{s}{\sqrt{n}}.$$

The standard error of the mean of the plate counts by this relationship is calculated as follows:

$$s_M = 14.7/\sqrt{15} = 3.8 \text{ bact/ml.}$$

In accordance with the definition of standard error (or deviation)

there exists a better than fifty-fifty chance that the true mean lies between 146 and 154 bact/ml.

The example, therefore, illustrates how the standard deviation may be used to establish the reliability of the mean.

Reliability of Derived Quantities. Frequently it is desired to form a quantitative estimate of the cumulative effect upon an analytical result of the individual errors involved in the determination. In a typical determination of a constituent of water, the individual errors may stem from (1) sampling; (2) inaccuracies in weighing, titration, preparation and manipulation of standard solutions and color standards, and (3) inherent inaccuracies of the analytical method. In forming an estimate of the error in the final result, the following rules are useful:

1. The standard error of a sum (or difference) is the sum of the standard errors in the individual items involved in the addition (or subtraction).

2. The relative standard error in a product or quotient is the sum of the relative standard errors of the items involved in the multiplication (or division).

With these rules, it is possible to form a quantitative estimate of the final overall error. The analysis is particularly useful in determining the permissible share of error that may be made in each individual step of a laboratory procedure, so as to maintain the overall error of the result within desired limits.

Example 3. The alkalinity of a finished water is measured by taking a 100-ml sample and adding N/50 sulfuric acid to methyl orange end-point. A total of 1.7 ml of acid is added before the pinkish color appears, denoting the titration end-point. The alkalinity of the sample is then calculated by the formula,

$$\text{Alkalinity} = \frac{50{,}000\ (\text{Vol. acid}) \times (\text{Normality of acid})}{(\text{Vol. of Sample})}$$

$$\text{Alkalinity} = \frac{50{,}000(1.7) \times \left(\frac{1}{50}\right)}{100} = 17 \text{ ppm}$$

Assume that the per cent standard errors of the various items entering into the calculation are as follows:

(i) measurement of acid from burette, 6%;
(ii) measurement of volume of sample, 2%;
(iii) normality of standard acid, 4%.

Then, according to the rule for standard errors of products and quotients, the standard error of the determination is $6 + 2 + 4 = 12\%$. Accordingly, the alkalinity is

$$17 \pm 0.12(17) = 17 \pm 2 \text{ ppm}$$

That is, a better than fifty-fifty chance exists that the true alkalinity lies in the range 15 to 19 ppm.

Comparison of Two Series. Using the mean and the standard deviation, it is possible to examine two similar series and ascertain whether they differ significantly. The water-works chemist may wish to compare the results of a determination of a water constituent using two different analytical procedures. In another instance he might desire to make laboratory studies to find out whether a longer period of mixing, after chemical dosage, would result in significantly better color removals from raw water. In all investigations of this sort, it is necessary to conduct two series of tests simultaneously, using each day the same raw water sample in both and noting results. Often it is found that a clear-cut distinction in results does not exist; sampling fluctuations may obscure the effect of the difference in treatment, so that a definitive answer is not forthcoming—at least in a reasonable length of time. In this event resort may be had to a statistical method that lends considerable aid to the judgment. The method is illustrated by an example.

Example 4. It is desired to compare results obtained for the concentration of carbon dioxide, CO_2, by two methods:

(1) Usual method of titration to phenolphthalein end-point; and
(2) Calculation of CO_2 from observed values of pH and alkalinity, using the carbonate-equilibrium equation. [Moore, Jour. A. W. W. A., **31**, 51 (1939)]

Results for CO_2 by the two methods for ten successive days are the following:

Method (1)—titration: 10, 11, 8, 7, 12, 10, 9, 9, 7, 10; Ave. = 9.3
Method (2)—calculation: 9, 9, 10, 9, 13, 8, 11, 11, 7, 9; Ave. = 9.6

It is seen that the average value by the second method exceeds that by the first. Can it safely be inferred from these results that the calculated value of CO_2 is higher than that given by direct measurement? In order to compare the two series statistically, it is necessary to calculate a quantity "t" as given by the following formula:

$$t = \frac{M_2 - M_1}{\sqrt{\frac{s_1^2 + s_2^2}{N - 1}}}$$

where M_1, M_2, s_1 and s_2 are the means and standard deviations of the two series and N is the number of items in each series.

Numerical values are:

$M_1 = 9.3$ $\quad s_1 = 1.55$
$M_2 = 9.6$ $\quad s_2 = 1.62$ $\quad N = 10$

Therefore,

$$t = \frac{9.6 - 9.3}{\sqrt{\frac{1.55^2 + 1.62^2}{10 - 1}}} = 0.400.$$

The question of whether or not the two series differ significantly may then be decided by reference to the following table:

VALUES OF t FOR A 95 PER CENT LEVEL OF SIGNIFICANCE

N	t	N	t	N	t
2	2.92	7	1.78	12	1.72
3	2.13	8	1.76	13	1.71
4	1.94	9	1.75	14	1.71
5	1.86	10	1.73	15	1.70
6	1.81	11	1.72	16	1.70
				large	1.64

From the formula for t, it is seen that the more divergent are the two series, the larger will be the value of t. If, for a given value of N, the calculated value of t is less than the corresponding value in the table, then the difference in the two series may not be considered significant. In the example, the calculated value of t (0.4) is considerably less than that in the table (1.73) corresponding to $N = 10$. Hence the experiment definitely does not indicate a significant difference in the values obtained for carbon dioxide by the two methods.

A somewhat more precise statement to the same effect may be made. On the basis of the hypothesis that the two methods do *not* differ significantly, only a 5 per cent chance exists that two series of N each will yield as high a value of t as given in the table, due to the influence of random sampling fluctuations.

Error analyses along the lines of Examples 2 and 3 may be applied to most determinations made in water-works laboratories. Some determinations, however, are not amenable to simple calculation. Foremost among these is the evaluation of bacterial density from fermentation-tube tests according to the "most probable number" concept.

Nomogram for Determination of "Most Probable Number" of Bacteria. An alignment chart has been developed to facilitate the evaluation of MPN values from all types of fermentation-tube tests involving three consecutive decimal dilutions. The chart may be applied to tests with any number of tubes, both positive and negative in each of the three dilutions. The method is indicated by an example worked out upon the chart (Fig. 2).

Use of Nomogram. The alignment chart may be applied to all tests with any number of tubes, both positive and negative, in each

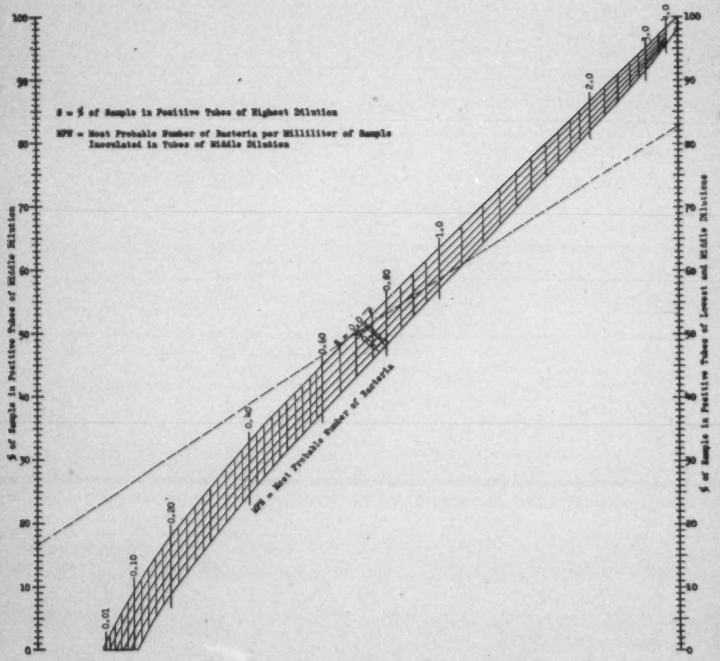
P = % of Sample in Positive Tubes of Highest Dilution
MPN = Most Probable Number of Bacteria per Milliliter of Sample Inoculated in Tubes of Middle Dilution
% of Sample in Positive Tubes of Middle Dilution
% of Sample in Positive Tubes of Lowest and Middle Dilutions
MPN = Most Probable Number of Bacteria
0.01
0.10
0.20
0.30
0.40
0.60
0.80
1.0
2.0
3.0
4.0

FIG. 2.—MOST PROBABLE NUMBER OF BACTERIA FROM FERMENTATION-TUBE TESTS INVOLVING THREE CONSECUTIVE DECIMAL DILUTIONS

of three consecutive decimal dilutions. Bacterial densities are given in terms of the "most probable number" per milliliter inoculated in tubes of middle dilution. Tubes of the *lowest* dilution contain the *greatest* volume of sample.

Example:

1 ml	0.10 ml	0.01 ml
2+	5+	1+
0—	5—	1—

Total volume of sample = 3.02 ml.
% volume in + tubes of 1-ml dilution = 100 × 2/3.02 = 66.2%.
% volume in + tubes of 0.10-ml dilution = 100 × 0.5/3.02 = 16.6%.
% volume in + tubes of 1-ml and 0.10-ml dilutions = 66.2% + 16.6 % = 82.8%.
% volume in + tubes of 0.01-ml dilution = 100 × 0.01/3.02 = 0.33%.

Draw a straight line (see dashed line on graph) connecting point 16.6% on left-hand scale with point 82.8% on right-hand scale. Read the corresponding "most probable number" at intersection of straight line and curve (interpolated) for $S = 0.33\%$.

MPN = 0.83 bact in 0.10 ml or
= 8.3 bact/ml

Answer.

METROPOLITAN WATER DISTRICT FINANCING AND THE COST OF METROPOLITAN WATER

BY KARL R. KENNISON*

[*Read March 21, 1946.*]

ON September 25, 1941, the author presented to the Association a paper on the subject, "Water Charges to Municipalities in the Boston Area by the Metropolitan District Commission". It was published in the Journal for December, 1941.‡ Changes have occurred since that time in the financial structure of the District, in the method of making assessments for water, and in the cost as measured by these assessments, some of which changes were predicted and recommended in the original paper. In view of recent developments and the current wide interest on the part of many communities which could advantageously join the District, this is an opportune time to present further data, which will bring the matter up to date and which will explain the effect of recent legislation on the financial set-up.

Late in 1941, a special legislative recess commission was appointed, primarily to study the possibility of extending the use of the new water-supply sources to include additional municipalities. This recess commission held a number of hearings and collected a great deal of data. It determined that the principal obstacle to enlargement of the District was the cost of Metropolitan water, which at that time averaged nearly $90 per mil gal. This obstacle was a potent one, in spite of the fact that Chapter 727, enacted October 31, 1941, had materially reduced the entrance fees charged to new members and had provided for the assessment of stand-by charges against non-member towns having connections with the system, which incidentally was in line with suggestions by the author in his 1941 paper.

The recess commission filed its report as House Document 1334 of 1943. This report contains many items of interest, including an

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‡This Journal, 55:4, 522, Dec., 1941.

analysis of the use to date made of the new Quabbin source, but for which the "bottom" would have been pulled out of Wachusett Reservoir in 1941, and this in spite of the failure of the District to expand. One of the conclusions drawn was that the cost of Metropolitan water must be decreased to an average or base price not in excess of $60 per mil gal before new members would be attracted to join and give up their local supplies. Legislation was proposed, but not passed, which would give such assurance to new members. Legislation was also proposed, but not passed, which, by annually issuing quasi-refinancing bonds to the extent that capital requirements may exceed the fixed sum of $2,750,000, would immediately reduce the base or average cost of water to about $60. Legislation was also proposed, but not passed, fixing the price for water delivered directly from the reservoir and aqueduct system: $45 from Quabbin Reservoir and $60 from the Wachusett-Sudbury system.

The bill actually passed as a result of the recess commission's proposals was Chapter 543, enacted June 12, 1943, which (1) extended eligibility to membership in the District from the 10-mile radius to the 15-mile radius, to the extent that the District had extended or can reasonably extend its distribution system; (2) reduced the stand-by charge from 0.030 to 0.015 of one per cent of the valuation of any town capable of being supplied from the District's distribution system which continues to be found by the Department of Public Health to have an inadequate supply or which continues to maintain a connection; (3) eliminated entrance fees entirely in the case of towns joining and taking their entire supply from the District, and (4) fixed the price of water from the distribution system to eligible non-members at a $75 base, varied in accordance with the practice of proportioning 2/3 on consumption and 1/3 on valuation. Although no addition of new members resulted from this legislation, widespread interest was aroused and several meetings were held in 1944 of a committee appointed by the Governor, consisting of two representatives each from Boston, Cambridge, Newton, Belmont, Braintree, Brookline, Saugus and Westwood. Its first meeting was attended also by representatives from 35 other communities in the Metropolitan area.

Two subcommittees, one on finance and one on technical matters, were appointed, consisting of representatives designated by four of

the municipalities most interested. The subcommittee on technical matters consisted of Thomas R. Camp of Cambridge, Chairman, Walter B. Bushway of Brookline, Robert P. Shea of Boston and the author, of Newton (the first two, in addition to the author, being members of this Association). This committee was largely concerned with legislative proposals which would induce towns taking their local supplies from the drainage area of the Charles River to abandon them in favor of the Metropolitan Water District and thus, incidentally, take an important first step in sweetening the waters of the Charles River Basin, in which all towns in the Metropolitan area are heavily involved financially. This subcommittee made many suggestions which were incorporated in the subsequent legislation, referred to below.

The subcommittee on finance consisted of Charles J. Fox of Boston, Chairman, Lucius T. Hill of Brookline, Clyde O. Ruggles of Cambridge and Clarence C. Colby of Newton. The work of this committee was more directly related to the subject of this paper. It made a thorough study of the possibility of effecting an immediate reduction in the average cost of water by annual bond issues under the methods which had been proposed the previous year by the recess commission. This subcommittee on finance made recommendations which differ in some respects from the legislation finally enacted. Its report is particularly important to our understanding of water district financing and is briefly abstracted as follows:—

The failure of potential members to utilize the exceptional facilities now available is primarily due to the fact that the construction involved in developing the supply was financed by relatively short-term bonds. The new works are certainly as permanent as those making up the original District facilities and yet have been financed in the main by 30-year serial bonds with an average maturity of 15 years as compared with 40-year sinking-fund bonds for the old works. The heavy capital charges resulting from this ultra-conservative financing of the new works have placed the cost of water to members of the District at a considerably higher figure than the cost to non-members from their present independent systems. It is apparent that in order to induce these non-members to join the Metropolitan Water District steps must be taken to bring the cost of water furnished by the District to a level more closely approximating the present costs claimed by non-members.

Since capital charges constitute the important factor in the cost figure of which non-members are critical, it would appear logical to take steps to reduce

the present effect of such charges on the annual assessment to members of the District. In view of the life of the improvements involved in these capital charges, such a step would merely be a desirable corrective in the original plan of financing. As stated in the report of the recess commission, the present generation is called upon under the current financing arrangement to finance works which will be available for many years without the future generations being properly assessed for the benefits derived. The question has been investigated of the extent to which new bond issues can accomplish a reduction in the average or base cost per million gallons assessed against the various municipalities in the Water District, on the assumption that new customers to the extent of about 25 mgd will be secured through lower water costs and that new construction bonds will be required in the aggregate sum of about $11,000,000 for improvement of distribution facilities, in addition to those already authorized. The conclusions are that:—

To reduce the cost from the present $80, more or less, per mil gal to	Bonds for this purpose, aggregating	Would have to be issued commencing in 1946 and covering a period of
$55,	5 to 6 million dollars	10 to 11 years
50,	12 to 13 " "	15 to 16 "
45,	22 to 23 " "	18 to 19 "
40,	36 to 37 " "	23 to 24 "
35,	About 58 " "	About 50 "

The subcommittee is in agreement that it is financially impracticable to aim at an average or base cost of less than $45 per mil gal.

Since the purpose of any plan of this sort is for the development of a wider use of the District's sources of supply, any new bonds issued in this connection should definitely indicate this purpose; and to this end it is recommended that they be designated as Water-Use-Development Bonds. To emphasize further the true nature of this financing, the committee has deemed it desirable to make the commencement of this water-use-development program dependent upon the addition, to the ranks of those municipalities taking their entire supply from the District, of new members, or existing members, to the extent of 10 mgd measured in average consumption of water in the previous calendar year. In other words, the program which the committee has in mind will not go into effect until 10 mgd in new customers appears. For example:—

If enough new customers for $45 water start the financing program in	The aggregate amount of bonds required would be	Covering a period of
1946	22 to 23 million dollars	18 to 19 years
1948	16 to 17 " "	15 to 16 "
1950	11 to 12 " "	13 to 14 "

Based on the assumption that new customers to the extent of 10 mgd start the financing program off in 1946 and that in the next two or three years this new consumption will increase to about 25 mgd, it is estimated that, in order to reduce the base cost to $45, the criterion to be used by the State Treasurer in determining the amount of the new bonds should be the inclusion in the total annual assessment of capital charges limited to a sliding scale of $1,300,000 in 1946, gradually increasing to a maximum of $2,000,000 in 1956. Failure of the estimated consumption to be realized will, of course, affect the cost per mil gal in direct proportion. For example, it will take a reduction of four or five mgd in the estimated total consumption to affect adversely the cost per mil gal by $1.00.

Assessments for water on members of the District have heretofore been based two-thirds on water consumption and one-third on valuation. As this formula works out, municipalities of high valuation pay in some cases materially more than those with low valuation when expressed in terms of dollars per mil gal. Some municipalities pay, roughly, ten per cent less than the average cost, while others pay nearly fifty per cent more than the average cost. If the present method of apportioning were continued, the offer of $45 water to new members would tend to be ineffective, since the actual price to municipalities of high valuation would be considerably in excess of $45, thus militating against full attainment of the objectives sought. The committee feels that when this program starts the annual assessment should be based solely on consumption, which would mean uniform treatment for all members.

In the meantime, the subcommittee on technical matters had included in its report certain recommendations which would affect the cost of Metropolitan water to municipalities like Cambridge, Newton and Brookline, and had considered the possibility that a portion of the local works of such municipalities might be taken over. In the event that they should take their entire supply from the District, it proposed that:—

In order to make it convenient for the District to take over these works without the expenditure of actual funds, and for the communities to receive compensation in their water departments without the receipt of actual funds, compensation should be made in the form of credits on their annual District water assessments. It is proposed that the annual credits be fixed at a sum which will amortize the principal in 25 years at 1½% interest.

The subcommittee on finance called to the attention of the Governor's Committee the fact that, with credits applied as suggested by the subcommittee on technical affairs, the taking over by the District of certain local works of Cambridge, Newton and Brookline

could easily result in a material reduction to these municipalities from the recommended figure of $45 per mil gal, and that each million dollars of such gross credits amortized as suggested would add only about $0.60 per mil gal to the base or average cost throughout the District.

After considering its subcommittees' reports, the Governor's Committee concurred in their recommendations, except that, in order to make the bid for new customers more effective, it concluded to propose legislation, further reducing the cost to $40 per mil gal. and furthermore proposed not only fixing this as a limit entirely independent of the total consumption in the District but also starting the program in 1946, regardless of whether or not any new customers should show up.

The bill actually passed as a result of the recommendations of the Governor's Committee was Chapter 587, enacted July 12, 1945, which (1) allows water supply connections between member and non-member towns without restriction and eliminates the stand-by charge to non-member towns, leaving the question of their connection with, and their supply from, the District's distribution system entirely a matter of approval by the State Department of Public Health; (2) clarifies the liability of all new users to pay, over a period of 10 years, if desired, the cost of connection to the District's distribution system; (3) eliminates any difference between the price of water to members and the price to non-members in the Metropolitan area; (4) provides for optional agreements between the District and towns which do enter, under which the Commission may acquire water supply works and lands of the town which are of value for any purposes of the Commission, its Sewerage and Parks Divisions as well as its Water Division (such works are to be taken over at cost, which if not agreed upon shall be determined by appraisal commissioners appointed by the Supreme Judicial Court); (5) provides that, whether or not such abandoned works are acquired by the District, they may be disposed of without restriction on account of prior dedication to water supply purposes; (6) provides that works so taken on account of their usefulness to the Sewerage or Parks Divisions of the Commission shall be compensated for by assessments upon the towns in the Sewerage or Parks districts respectively, and not upon the towns in the

Water District; (7) makes adequate provision for the transfer to the Metropolitan District Commission, without loss of pay or impairment of civil service status, of employees from the Water Departments of towns whose facilities are abandoned upon entry into the District, and (8) provides for a reduction, commencing in 1946, in the water assessments, by issuing annually so-called Water-Use-Development Bonds, referred to above as quasi-refinancing bonds, so that the result is a fixed price of $40 per mil gal to all towns supplied from the distribution system, regardless of how much they take and irrespective of valuation, which has formerly resulted in wide discrepancies in the rate per mil gal. The consumption basis of assessment continues, of necessity, to be the average rate of consumption during the previous calendar year, although the assessment is, as it always has been, in payment for use during the year of assessment.

In answer to criticism, brought to the author's attention, that the wording of the statute is misleading with respect to the certainty of the $40 price, suffice it to say that, although any excess cost would have to be assessed against the members of the district by the provisions of Sec. 26 of Chapter 92 of the General Laws, this possibility is eliminated by the new Section 26A, which ensures that there can be no excess over the $40 price. In substantiation thereof, the Attorney General, in a ruling given to the Metropolitan District Commission on March 11, 1946, states that "the price of water to members and municipalities eligible for membership in 1946, should be $40.00 per million gallons measured by the consumption for the preceding year, as provided in said Section 26A." The present session of the legislature may clarify the statute but, on the basis of proposals filed to date, is not expected to alter the provisions as outlined above. Table 12 shows the cost of Metropolitan water to the municipalities that are members of the Water District and the reduction effected by Chapter 587 of 1945.

It is a remarkable fact that the soundness of the Water District's financial structure permits such a guarantee of $40 water. The accompanying graphs illustrate what can reasonably be expected. The estimates for the future are based on an assumption that the present population of the 20 cities and towns now members of the Water District will increase from 1,558,287 in 1945 to a ceiling of 1,800,000

TABLE 12.—COST OF METROPOLITAN WATER TO THE MUNICIPALITIES IN THE DISTRICT.

	Assessment against members of the Water District		Average mgd taken from District sources	Approx. cost per mil gal, using the previous year's consumption, as is necessarily done when assessment is levied			
	1945	1946 (tentative)	1945	1943	1944	1945	1946
Arlington	$ 83,105	$ 35,721	2.447	$105	$ 99	$ 91	$40
Belmont	66,502	25,756	1.764	116	118	106	40
Boston	2,908,331	1,615,872	110.676	82	77	73	40
Brookline	61,249	9,283	0.636	515	422	265	40
Chelsea	105,122	62,424	4.276	78	75	71	40
Everett	179,498	104,105	7.130	78	74	70	40
Lexington	31,665	11,811	0.809	119	108	102	40
Malden	132,090	68,653	4.702	88	84	80	40
Medford	134,505	59,480	4.074	96	94	85	40
Melrose	54,476	22,230	1.523	104	103	98	40
Milton	46,770	14,370	0.984	128	122	119	40
Nahant	8,467	3,415	0.234	103	98	93	40
Newton	32,044*	290	0.020	5,780	855	445	40
Quincy	195,695	88,241	6.044	98	94	90	40
Revere	70,957	37,750	2.586	88	83	79	40
Somerville	271,153	159,186	10.903	76	73	69	40
Stoneham	23,903	9,394	0.643	101	96	87	40
Swampscott	32,666	12,543	0.859	109	104	100	40
Watertown	85,954	36,842	2.523	86	84	87	40
Winthrop	42,100	20,362	1.395	89	85	82	40
	$4,568,082	$2,397,728	164.228	$86	$81	$77	$40

*In addition to this sum, $5,850 was billed under agreement of November 4, 1925.

by 1970, an increase at the rate of about 15½% in the next 25 years. This may be compared with an increase of 20¾% during the last 25 years, which included the depression years, and with an increase of 66% in the 25 years prior to that. The estimates are also based on an assumption that, during the next 25 years, the consumption per capita per day will increase from 112 gal in 1945 to 120 in 1970, only 8 more in spite of the fact that the increase, after the services were 100% metered in the early 1930's, was from about 90 to 112. These estimates seem to be sufficiently conservative as a basis for a study of the District financing.

As to the addition of new members to the Water District, it is considered reasonably conservative to assume not much more than 30 mgd worth of new customers. Cambridge represents the majority

of this and computations have also been made, and shown on one of the graphs, to enable a comparison to be made between the condition with Cambridge in and the condition with Cambridge out—that is, continuing to use its local sources to the limit.

The principal purpose of the graphs is to show the extent to which it will be necessary, in order to reduce the price to $40 per mil gal and keep it there, to issue the water-use-development bonds which Chapter 587 of last year provides shall be issued annually as 30-year serial bonds, and also to show their effect on the debt structure.

Figure 1 shows the condition under existing legislation. However, as far as the requirements of new construction are concerned, the Commission states by its filing of a new bill this year, House Document 1354, that a post-war additional authorization of $10,000,000 is necessary to complete the city tunnel extension of its Hultman Aqueduct to Chestnut Hill and to construct a much-needed distributing reservoir and other new works. Hence, Figure 2 was prepared to show what would be the effect of the passage of this bill, which not only authorizes the additional issue of $10,000,000 worth of construction bonds, but also increases the term of all future serial bonds for construction from 30 years to 50 years. A comparison of Fig. 1 with Fig. 2 brings out the fact that the aggregate total, $40,150,000, of the water-use-development bonds required in the case of the proposed additional authorization of $10,000,000 is only slightly more than the total, $39,340,000, required if Ho. 1354 is not passed; and also the issuing of the bonds does not extend over any longer period of time, the requirements being practically the same in both cases—namely, 1946 to 1969, inclusive.

The reason for this is that, during the period in question, the annual requirements for principal and interest on the $10,000,000 worth of new construction bonds, issued as 50-year serial bonds, as proposed in the bill, and at 1½% interest, as unanimously agreed by last year's subcommittee on finance, are about $335,000 a year, which is largely offset by the following: (1) if, because of lack of funds, the city tunnel is not completed, Newton cannot be supplied as proposed through one of the shafts and will probably continue its local source, and the assessment thus lost to the District will amount to

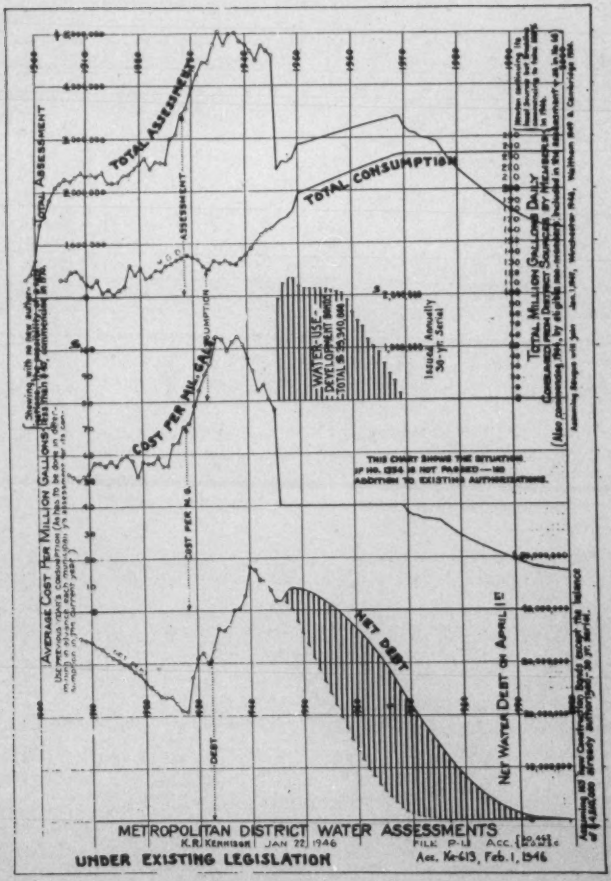
TOTAL ASSESSMENT
TOTAL CONSUMPTION
COST PER M.G.
NET DEBT
WATER-USE DEVELOPMENT AND TOTAL ESTIMATES
Issued Annually 30-yr Serial
THIS CHART SHOWS THE SITUATION IF NO. 1354 IS NOT PASSED — NO ADDITION TO EXISTING AUTHORIZATIONS.
AVERAGE COST PER MILLION GALLONS
TOTAL MILLION GALLONS DAILY CONSUMED FROM DISTINCT SOURCES BY METROPOLITAN WATER DISTRICT
NET WATER DEBT ON APRIL 1ST
METROPOLITAN DISTRICT WATER ASSESSMENTS
UNDER EXISTING LEGISLATION
K.R. KENNISON JAN 22 1946
FILE P-13 ACC. 29,551-c
Acc. K-613, Feb. 1, 1946

FIG. 1.

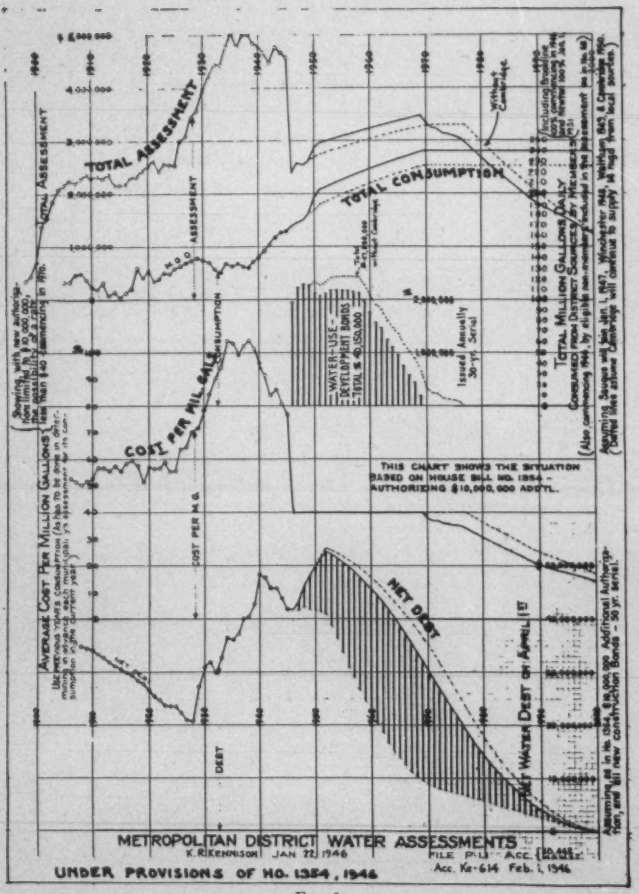
TOTAL ASSESSMENT
TOTAL CONSUMPTION
COST PER MIL. GALS.
NET DEBT
THIS CHART SHOWS THE SITUATION BASED ON HOUSE BILL NO. 1384 - AUTHORIZING $10,000,000 ADDTL.
METROPOLITAN DISTRICT WATER ASSESSMENTS
UNDER PROVISIONS OF HO. 1384, 1946

FIG. 2.

approximately $70,000 a year; (2) the impossibility of discontinuing the pumping at Chestnut Hill about 1950, on account of non-completion of the pressure tunnel, will make it impossible to effect an annual saving of at least $140,000; (3) if all new construction bonds are continued on a 30-year basis, instead of 50 years as proposed in the bill, the additional requirements for principal and interest, during the period in question, on the remaining $4,810,000 already authorized but not yet issued will be about $60,000 per year.

These graphs also show the soundness of the financial structure, since, in any event, the net water debt is bound to decrease rapidly after about 6 years. They also show that, although there is no provision in Chapter 587 for ever reducing the cost below $40, it may be possible to effect such a reduction, as soon as the necessity for the annual issue of water-use-development bonds is past, and this could occur after about 25 years or, at most, after about 30 years.

Incidentally, the effect of Cambridge being in or out is shown on Fig. 2. If Cambridge, instead of joining the district about 1950, keeps its local supply, the result will be an increase of roughly 20% in the aggregate total of water-use-development bonds required.

Figure 3 has been prepared to answer the question that may very properly be asked: "What if it is necessary to keep on appropriating additional amounts for new construction, for example, to extend the pressure tunnel to the northern high service and eliminate Spot Pond pumping?" This graph shows that an additional $10,000,000 could be authorized every 15 years and still the aggregate total of water-use-development bonds required, $41,950,000, represents an increase of only about 5%. This is because the principal effect of such continued future construction is merely to maintain more nearly the $40 rate and lessen the possibility, above referred to, of decreasing it after about 30 years. In fact, if the rate is never to be allowed to fall below $40, there is obviously room for a considerable amount of additional construction in the future. For example, an assumed $10,000,000 every 15 years corresponds to a future maintenance of the water debt generally below $20,000,000—the low point it reached in 1928, prior to the heavy expenditures for the Quabbin project.

Figure 4 has been prepared, merely for comparative purposes, to show what the situation would be without any water-use-development

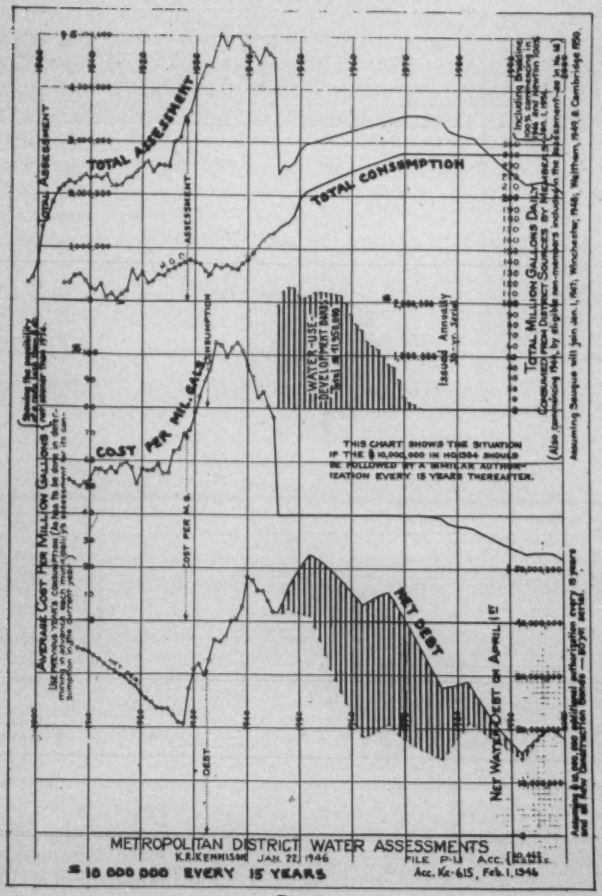
TOTAL ASSESSMENT
TOTAL CONSUMPTION
COST PER MIL. GALS.
WATER-USE DEVELOPMENT BONDS
Issued Annually
Total $41,955,000
THIS CHART SHOWS THE SITUATION IF THE $10,000,000 IN HOUSE 384 SHOULD BE FOLLOWED BY A SIMILAR AUTHORIZATION EVERY 15 YEARS THEREAFTER.
NET DEBT
NET WATER DEBT ON APRIL 1ST
METROPOLITAN DISTRICT WATER ASSESSMENTS
K.R.K. EMMISON JAN. 22, 1946
FILE P-U ACC. [illegible]
Acc. Ke-615, Feb. 1, 1946
= 10 000 000 EVERY 15 YEARS

FIG. 3.

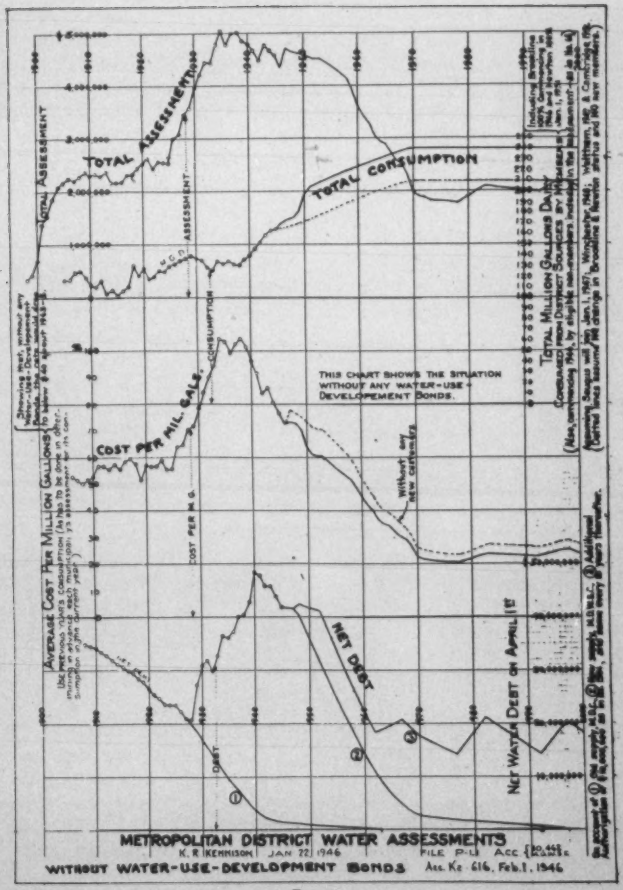
TOTAL ASSESSMENT
TOTAL CONSUMPTION
COST PER MIL. GALS.
THIS CHART SHOWS THE SITUATION WITHOUT ANY WATER-USE-DEVELOPMENT BONDS.
NET DEBT
NET WATER DEBT ON APRIL 1ST
METROPOLITAN DISTRICT WATER ASSESSMENTS
WITHOUT WATER-USE-DEVELOPMENT BONDS
K. R. KENNISON JAN 22 1946
FILE P-L1 ACC
Acc. Ke 616, Feb. 1. 1946

FIG. 4.

bonds—in other words, if the provisions for this so-called refinancing had never been included in Chapter 587. In such case, the incentive to new users is removed and the graph shows the situation both with and without the addition of new customers. This graph includes the same assumption of future authorizations, $10,000,000 every 15 years, and illustrates the ultimate certainty and rapidity of a drop in the assessments and in the cost per million gallons, the $40 rate being reached about 1963 to 1965, depending upon the number of new users.

Incidentally, this graph also contains an analysis of the net debt and its division between that due to the old Wachusett supply, the new Quabbin supply as authorized to date, and additional authorizations. It should be clear from these graphs that the net debt will drop again to the 1928 low of about $20,000,000 in about 15 years, except for the added debt due to the water-use-development bonds, which will materially increase the debt during the next 40 years. If it were not for these so-called refinancing bonds, the cost per million gallons would probably drop even as low as $25 to $30 by the year 1970 and thereafter would probably not exceed this figure.

Several tables have been prepared to complete the statistical information originally presented.

Table 3-A, showing the annual assessments, brings up to date Table 3 on page 528 of the original 1941 paper. Note that there were additional expenditures during the war years and also in the post-war years, which were not originally foreseen. This table is based, like Fig. 3, on an assumed new authorization of $10,000,000 worth of 50-year serial bonds, every 15 years.

Table 4-A, showing the status of sinking-fund bonds, brings up to date Table 4 on page 532 of the original 1941 paper. Actually, the sinking fund reached the point two years ago where it was more than ample to pay off all the outstanding sinking-fund bonds; and one of the recommendations of the Governor's Committee which was enacted was that, commencing in 1946, the surplus and also all future receipts from sales, etc., should annually apply to a reduction of the amount of the water-use-development bonds to be issued to maintain $40 water. The estimated surplus to be so credited is shown in the last column.

TABLE 3-A.—ANNUAL ASSESSMENTS OF THE METROPOLITAN WATER DISTRICT.

	For maintenance and all other expenditures except capital expenditures	For bonds, all principal and interest and pay-as-you-go capital expenditures				Credits		Total (equivalent to $40 per m.g., 1946-1973)
		Construction by Metropolitan District Commission of old supply and distribution works	Construction by Metropolitan District Water Supply Commission	Possible future construction bonds	Principal and interest requirements of water-use-development bonds	Proceeds of water-use-development bonds	Stand-by charges, 1943-45. Sinking-fund surplus and misc. receipts commencing 1946	
1940	$ 986,385	$1,226,527	$2,573,003					$4,785,945
1941	1,005,090	1,031,714	2,631,676					4,668,480
1942	1,108,494	714,179	2,659,872					4,482,545
1943	1,635,475	547,521	2,649,618				$ 72,868	4,759,746
1944	1,376,957	489,971	2,834,728				36,434	4,665,222
1945	1,166,584	333,532	3,104,299				36,333	4,568,082
Estimated								
1946	1,320,000	461,734	3,100,266			$1,934,000	550,000	2,398,000
Chestnut Hill pumping stopped								
1950	1,200,000	395,000	3,113,000		$ 392,000	2,110,000	130,000	2,860,000
1955	1,205,000	344,000	3,020,000		878,000	2,182,000	185,000	3,080,000
1960	1,205,000	239,000	2,395,000		1,336,000	1,760,000	185,000	3,230,000
1965	1,205,000	100,000	1,629,000	$139,000	1,609,000	1,117,000	185,000	3,380,000
Spot Pond pumping stopped								
1970	1,167,000	100,000	558,000	337,000	1,723,000	210,000	185,000	3,490,000
1975	1,167,000	100,000	406,000	322,000	1,648,000		185,000	3,458,000
1980	1,167,000	100,000	383,000	446,000	1,259,000		185,000	3,170,000

TABLE 4-A.—SINKING-FUND BONDS FOR CONSTRUCTION OF OLD SUPPLY.

	Amount of loan paid off	Assessed requirements		Net debt April 1	Estimated surplus to be credited each year
		Fund	Interest		
1941	$10,000,000	$36,773	$520,685	$992,195	
1942	3,500,000	20,742	301,685	634,170	
1943	2,000,000	———	205,435	254,755	
1944	2,000,000	———	135,435	———	
1945	650,000	———	89,060	———	
1946	1,350,000	———	54,060	———	$550,000
	To be paid off				
1947	———	———	30,435	———	165,000
1948	———	———	30,435	———	180,000
1949	398,000	———	23,968	———	185,000
1950	500,000	———	8,750	———	130,000

The original Table 5 on page 534 needs no elaboration, except to state that the actual amount of pay-as-you-go expenditures assessed for the construction of additions and improvements in the old supply and distribution works was $200,000 in 1942, $161,000 in 1943, $176,000 in 1944 and $72,917 in 1945.

There is no point in presenting further general cost data in elaboration of the original Table 6 on page 538, until the city tunnel extension of Hultman Aqueduct, which was held up by the war, and other appurtenant works are completed.

There is little to be gained in presenting further data in elaboration of the original Table 7 on page 540, except to say that no new bonds for water supply construction have been issued during the war years since 1941 and that future issues will depend on the action of the present legislature on the proposal in House bill 1354, referred to above. However, Table 7-A supplements the original Table 7 to

TABLE 7-A.—SERIAL BONDS FOR NEW WARE-SWIFT SUPPLY, PRESSURE AQUEDUCT, ETC., METROPOLITAN WATER DISTRICT.

	Assessed requirements		Net debt April 1
	Principal	Interest	
1941	$1,432,000	$1,238,753	$44,757,000
1942	1,427,000	1,209,605	43,330,000
1943	1,489,000	1,191,875	43,841,000
1944	1,689,000	1,143,705	42,352,000
1945	2,009,000	1,089,535	40,463,000
1946	2,069,000	1,031,266	38,454,000

TABLE 8-A.—GROWTH OF POPULATION IN THE METROPOLITAN WATER DISTRICT AND WATER CONSUMPTION IN MILLION GALLONS DAILY.

	Population	Gallons per capita daily	Total consumed (mgd)	Credit from local sources, Newton and Brookline (mgd)	Supplied to expected new members and others eligible to join (mgd)	Total supplied from the Metr. distribution system (mgd)	Supplied to non-members, such as Framingham, Natick, hospitals, etc. (mgd)	Supplied to Worcester by pumping from Wachusett area (mgd)	Total demand on District sources (mgd)
1940	1,511,667	98.7	149.16	— 9.68	0.57	140.05	3.46		143.51
1941		102.4	155.70	— 9.76	0.89	146.83	3.01	1.92	151.76
1942		105.4	161.28	— 9.77	0.61	152.12	3.38	9.36	164.86
1943		109.4	168.39	—10.09	0.90	159.20	3.51	4.16	166.87
1944		111.9	173.30	— 9.99	1.47	164.78	3.33	6.59	174.70
1945	1,558,287	111.8	174.16	— 9.93	1.33	165.56	3.31	0.82	169.69
Estimated									
1950	1,600,000	113	181	— 5	22	198	4	6	208
1955	1,660,000	115	191		23	214	4	8	226
1960	1,720,000	117	201		23	224	4	10	238
1965	1,770,000	119	210		24	234	4	10	248
1970	1,800,000	120	216		25	241	4	10	255

the extent of showing the requirements during the last few years of the outstanding serial bonds which have financed the new supply to date.

Table 8-A, which is an extension of, and brings up to date, Table 8 on page 542 in the original 1941 paper, presents data on the growth of the Water District during the last 5 years and estimates for the future, on the conservative basis which is desirable in the financial estimates.

Summarizing the information presented herewith, the financial condition of the Metropolitan Water District is sound and is well capable of absorbing the shock, if it may be called such, of the water-use-development bonds which are, in fact, quasi-refinancing bonds. The result is that the price of water delivered from the District's metropolitan distribution system can be expected to be $40 per mil gal not only during the next few years but for any period in the foreseeable future.

Discussion

Harold W. Griswold (Hartford, Conn.). There is such a great difference between the way that eastern Massachusetts and southeastern New York operate and finance that I think perhaps it would be interesting if Mr. Brush gave just a little discussion on this paper.

William W. Brush (New York, N. Y.). Mr. President and gentlemen, I was very much interested in following the presentation of Mr. Kennison on financing and the proposed changing of the basis upon which additional cities can come into this metropolitan water district.

The financing of the New York City system of additional supply has been on the basis of 50-year bonds with a sinking fund accumulated yearly with which to retire the bonds at maturity. That statement may not be true at the present time. I have not been connected officially with the New York system for nearly eleven years, but generally the water supply financing has been on a 50-year maturity for the bonds.

Data will be given on the cost of the water supply of the Catskill system as compared with the system for the Metropolitan District of Massachusetts. The New York City Catskill water, delivered to the

city limits but without distribution cost, was estimated to cost $100 a mil gal. For a period of over ten years Catskill water was sold to communities outside of New York at $100 a mil gal, which fully covered the interest charges, amortization of the bonds and the maintenance and operation of the system. These communities obtained New York system water on the very advantageous condition of paying for what they took, irrespective of the amount, as no stand-by charge was made. The communities had to pay the cost of making the connections between the Catskill supply and their own particular water distribution systems.

The people of New York at the present time are paying $200 per mil gal for metered water. Formerly, when the people outside were paying $100, the New York City people were paying $133 a mil gal, but that price in New York City included the distribution of the water. The additional $33 represented about the distribution cost.

I think that certainly this Metropolitan District of Massachusetts has been administered financially in a very conservative manner, as is traditional for a New Englander. However, I believe that the present plan is generally for the best interests of the people in this district. I also believe that the benefits to a community from using the Metropolitan District water supply are such that it is very desirable that a larger number should have those benefits. Also, the improvement in the Charles River water, resulting from stopping the draft on this river for water supplies, will be of value to a very large number of people, so that in every way the new financial plan appears to represent a most happy change.

HAROLD W. GRISWOLD. Thank you, Mr. Brush. Are there any more questions or discussion? [No response.]

You might be interested to know that the Metropolitan District of Hartford County, Connecticut, which is a small one, serving only 300,000 people, has a revenue of $145 a mil gal, of which nearly half goes for fixed charges. In other words, water at $70 per mil gal against the $40 that the member towns in eastern Massachusetts pay, which seems to be rather a favorable rate.

PROBLEMS OF THE SPRING OVERTURN IN STRATIFIED LAKES

BY EDWARD S. DEEVEY, JR.*

[*Read at Superintendents' and Chemists' Round Table, March 21, 1946.*]

I HAVE hesitated to prepare a formal, detailed paper on a limnological subject, for fear of missing your interests, about which Dr. Renn was commendably vague when he invited me to address you. He did suggest, however, that some of you are interested in the matter of the spring overturn in stratified lakes, for the plankton produced on such occasions is likely to produce noxious or unpleasant odors and flavors in water supplies. For want of a better lead, therefore, I have decided to explore this subject briefly and await your comments on this and other problems at the conclusion of my talk.

As you all know, the thermal cycle of a small lake in temperate latitudes is divided into four seasonal phases. (I shall speak of lakes deeper than about 10 meters, or 30 feet.) In the spring, as the ice melts, the whole column of water is ordinarily mixed to the bottom, partly by wind-induced turbulence and partly by convection. When the column warms up to 4° C., its temperature of maximum density, convection can no longer mix the warmer water into the underlying colder water and all mixing is by turbulence. As heating progresses, the relation of temperature and density of water is such that it becomes increasingly difficult for the wind to perform the necessary work of mixing and the ultimate result is the formation of a warm, fully circulating upper layer, the *epilimnion*, separated from a cold lower layer or *hypolimnion* by a region of sharp temperature gradient, the *thermocline*. This is the stage of *summer stratification* and it persists until cooling in the fall has advanced to the point where complete mixing is again possible. The period of *fall overturn* lasts until ice forms at the surface, when *winter stratification* sets in and the wind is prevented from mixing the cooler but lighter surface water into the bottom layers, which usually remain near 4° until the *spring overturn*.

*Woods Hole Oceanographic Institution, Woods Hole, Mass.

In summary, then, the annual cycle of such a lake includes two periods of full circulation and two of stratification, and the latter are, potentially at least, periods of *stagnation*. The elementary chemistry of stagnation, studied for many years by European and American limnologists, is based primarily on the distribution of oxygen in the hypolimnion. Oxygen is added to the lake by two agencies: the photosynthesis of aquatic plants and the diffusion of air into surface water. As the penetration of light, required for photosynthesis, is limited to small depths, and as diffusion without turbulence is an impossibly slow process, oxygen can be added to the deep water only by turbulent mixing, which takes place chiefly at the periods of overturn. This means that there is a net loss of oxygen in the hypolimnion during stagnation. The *rate* of loss depends principally on the production of organic matter in the surface waters—*i.e.*, on the amount of dead plankton and other organic detritus which falls through the thermocline, consuming oxygen in the process of decomposition. The *extent* of the loss, in terms of final oxygen concentration, depends on the total amount present in the lake at the overturn, especially on the ratio of the area of the hypolimnion to its volume. A deep lake with a large volume of water below a depth of about 10 meters will reach the end of summer stagnation with more oxygen remaining in this deep water than will a shallow lake in which the initial amount of oxygen is low. We find, then, two sorts of oxygen curves at full stagnation and their form is governed both by the total production of organic matter (the richness or productivity of the lake) and by the relative volume of the hypolimnion.

The advanced chemistry of stagnation has been developed very recently, as a result of studies on a very few lakes: Linsley Pond in Connecticut, Esthwaite Water in the English Lake District and the Schleinsee in Bavaria. All of them are small, fairly shallow and productive of much organic matter. Beginning with the knowledge that, during stagnation, not only is the oxygen depleted but various reduced substances, such as ferrous and ammonium bicarbonate, methane, hydrogen sulfide, etc., accumulate in the hypolimnion, it is possible to divide summer stagnation into three stages. (I shall deal with summer stagnation first, since for obvious reasons it has been better studied by limnologists). In Stage I, during early

summer, the oxygen in the hypolimnion falls to about 2 ppm and bicarbonates begin to accumulate. The oxidized surface of the mud, which is light brown due to ferric hydroxide, decreases during this stage from several centimeters to zero thickness. The boundary layer of oxidation in the mud may be defined by an oxidation-reduction potential of 0.20 volt and, when this value is found at the mud surface rather than at some depth below the surface, the oxidized layer may be said to have disappeared. In Stage II, as the 0.20-volt boundary rises into the water, the critical value for the reduction of ferric ion to ferrous is passed and ferrous iron and ammonia begin to accumulate in the lower water. The oxygen falls to very low levels and may not be detectible by the unmodified Winkler method. In Stage III, the processes of reduction continue at a slower rate and, if the stage lasts long enough, the "redox" potential at the mud surface falls to 0.10 volt, the critical level for sulfate reduction, and sulfides are precipitated.

At the fall overturn there is a rapid reversal of the processes just outlined. The readmission of oxygen into the hypolimnion leads to the oxidation of ferrous and ammonium compounds and ferric hydroxide is precipitated at the mud surface, re-forming the familiar, brown oxidized layer. The "redox" potential rises to 0.40 or 0.50 volt, values characteristic of oxygenated water, and the "redox" boundary for reducing conditions sinks several centimeters into the mud.[1]

In the sea the analogous process of overturn usually leads to bursts of phytoplankton production, for the nutrient substances, phosphate and nitrate, which have accumulated below the thermocline, are redistributed through the water column and made available to plankton. In the small lakes which have been studied, this mechanism seems to be quantitatively less important, probably for the reason that the iron in these lakes is more plentiful than in the sea and undergoes a more active cycle. Ferric phosphate is very insoluble—more so than ferric hydroxide—and at the fall overturn the phosphate is largely precipitated instead of being mobilized for plankton production.

The mechanism of the distribution of solutes in the hypolimnion

[1]My presentation of these events is intended to be purely descriptive. It may not be quite fair, for example, to say that the critical "redox" potential for ferrous ion is 0.20 volt, when all that we know is that ferrous ions appear at this level. The presence of the ferrous ions may instead be thought of as causing the observed potential. Little can be said about such matters until we know more about the role of micro-organisms in the metabolism of mud-water interfaces.

of small lakes has received some attention, though not so much as it deserves. It seems clear that vertical turbulence is not competent to account for such phenomena as the rate of heating and the accumulation of bicarbonate during stagnation. It has long been known that many lakes acquire heat near the bottom under an ice cover and, while convection can account for this so long as the temperatures are below 4°, some other means of exchange must be involved when heating takes place above 4°. The mechanism invoked is a system of density currents, which, arising in bottom water at shallow depths, flow down the slope into the hypolimnion. Such currents can be thermal during the early winter and in large lakes, as the bottom water is warmed to about 4° by radiation passing through the ice to the bottom of shallow bays and, becoming denser, seeks its own density level in mid-lake. Later, however, the density must be augmented by chemical means—*i.e.*, by the acquisition of bicarbonates and silicates from the mud—in order to continue the heating above 4°.[2] These density currents are analogous to those composed of silty bottom water flowing down the slope from the inlets of large reservoirs—Lake Mead, for example. They must flow in summer as well as in winter. Hutchinson has shown that the rate of increase of bicarbonate with time in the open water of Linsley Pond does not change regularly with depth but shows inflections, which are related to the ratio of mud area to water volume at a given depth. Unfortunately the evidence for density currents in small lakes is of this indirect sort, although attempts have been made to measure them directly.

Turning now to winter stagnation, we find that it has been less well studied than summer stagnation. What we do know suggests that the processes concerned are different in degree but not in kind. In Esthwaite Water, during seven weeks under ice, the spread of dissolved substances from the mud into the water was slower, the deoxygenation was less complete, and reduced conditions were confined to a narrower layer than during a corresponding length of time of summer stagnation. In this lake the oxygen concentration fell only to 4.2 ppm but in Linsley Pond winter values below 2 ppm are not unusual.

[2]The contribution of heat, stored in the mud during summer and delivered to the water during winter, must not be neglected in a general theory of the heating of lakes. Birge, Juday and March have shown that this source of heat is very important in Lake Mendota but it is improbable that it is so important in lakes with much lower hypolimnetic temperatures in summer.

Winter stagnation, if it is at all severe, as it seldom is in southern Connecticut and in England, can have several biological consequences. If the lake is shallow and highly productive of organic matter, oxygen depletion under ice may proceed so far that fish and other animals may suffocate. Winter fish-kills have recently received considerable attention from Greenbank, working in Michigan. He finds that they are not of regular occurrence but take place only in exceptionally hard winters, and then only if the ice is made opaque for long periods by the accumulation of snow. Ice by itself is ordinarily transparent enough to permit some photosynthesis and Greenbank recommends snow removal as a means of preventing fish-kills.

A second possible consequence of prolonged stagnation is that substances dissolved from the mud and accumulated in the deeper water—bicarbonates, silicates, etc.—may so increase the density of this water that the spring overturn may be incomplete. This appears to have happened in the spring of 1936 in Linsley Pond, after an unusually severe winter. If the products of summer stagnation are added to those of winter stagnation, the danger is that the lake may become permanently stagnant below the depth of effective mixing. An example of such a lake is Lake Mary in Wisconsin. Where such permanent stagnation exists, of course, it is much more usual to find that salt water has been added to the bottom of the lake, for example, by a saline spring or by a storm wave in the case of lakes near the seashore. Findenegg, however, has investigated several Austrian lakes, in which the incomplete mixing is due entirely to biochemical products and lasts for several years, or until a mild winter with no ice formation brings the stagnation to a close.

I can say little about the relation of the spring overturn to the production of different amounts and kinds of plankton, although this is the aspect of the subject in which you are presumably most interested. I have already pointed out that, although nutrients are among those substances which accumulate in the hypolimnion during stagnation, they are not necessarily available for increased plankton production at the overturn, owing to the loss of phosphate in the presence of appreciable quantities of iron. Spring bursts of phytoplankton, particularly of diatoms, are a usual feature of lakes but there is no reason to think that they are due to increase of nutrients, rather than to rising temperature or some other cause. There may be some

connection, however, between diatom growth and suspended ferrous and ferric iron, both of which are more abundant in surface waters at the times of overturn. Harvey has shown that particulate ferric hydroxide can be utilized by certain marine diatoms. Various other organisms are associated with the diatoms in the spring. Dinobryon usually appears as the diatoms are declining, and it has been thought that one predetermining condition for its appearance is low silicate concentration. But later work has shown that Dinobryon may also follow blooms of other organisms, such as Scenedesmus and Oscillatoria, which do not deplete the silicate as diatoms do. Synura, as I learn from Whipple, is a particularly noxious component of the plankton, which sometimes occurs in Massachusetts reservoirs in the spring and fall. I know nothing of its chemical requirements. The whole subject of the seasonal periodicity of plankton organisms is wrapped in mystery but it seems clear that it cannot be solved by paying attention solely to the inorganic chemistry and temperature of the lake. Biotic phenomena—by which I mean such factors as competition, grazing by zoöplankton, age of the population, accessory growth factors of vitamin nature and the possible rôle of antibiotics, analogous to streptomycin—must all be investigated. Chlorella cultures have been found to produce an antibiotic, but no antibiotics have yet been demonstrated for planktonic algae in nature, although their existence has been suspected.

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CORROSIVENESS OF WATER TO METALS

BY THOMAS R. CAMP*

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INTRODUCTION

THE basic theory underlying the electrochemical theory of corrosion of metals in water was first developed by Josiah Willard Gibbs of Yale University in his classic papers "On the Equilibrium of Heterogeneous Substances", published in the Transactions of the Connecticut Academy during the period from 1875 to 1878. Gibbs' great contributions to electrochemistry were not used to any considerable extent in this country until after the publication by Lewis and Randall in 1923 of their book, "Thermodynamics and Free Energy". Since 1923, a great mass of experimental data has been collected relating to free energies of chemical substances and single electrode potentials, much of which has been used in the evaluation of equilibrium constants.

It has long been known that the corrosion of metals in contact with water is dependent upon their single electrode potentials and the composition of the water. The "Electrochemical Theory of Corrosion" has been mentioned in the literature for many years, but it appears that the theory has not been developed to the point of being practically useful. It is the author's purpose to undertake this development and to illustrate the application of the theory by practical examples.

The paper is divided into two parts, to be published in consecutive issues of the Journal. "Part I, A Study of the Electrochemical Equilibria" deals with the theory and some simple applications. "Part II, Practical Applications of the Theory" will illustrate the usefulness of the theory with natural waters.

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PART I. A STUDY OF THE ELECTROCHEMICAL EQUILIBRIA

SYNOPSIS

Part I is an analysis of the electrochemical reactions which may take place in the corrosion of metals in contact with water. The equilibria are studied in terms of free energies and single electrode potentials. It is shown that all the reactions, including those resulting in the formation of solid corrosion products, can be explained in terms of half-cell reactions accompanied by the flow of electric current. A method is presented to determine the *corrosiveness* of a water to a particular metal and to determine which reactions will take place and what corrosion products will be formed. The method does not, however, present any means of determining the rate of corrosion.

CORROSION REACTIONS

Water is corrosive to a solid when it tends to dissolve the solid. The solution of a solid mineral, such as $CaCO_3$, is accompanied by its dispersion as positive and negative ions in solution. The solution of a solid non-polar compound, such as sugar, is accompanied by its dispersion as un-ionized molecules in solution. Neither of these cases involves a transfer of electrons to or from the dissolved substance and there is no flow of electricity. The *corrosiveness* of a water to solid mineral compounds or to non-polar compounds depends entirely upon its degree of saturation with the ions or molecules of the compound.

Water is corrosive to a solid metal when it tends to dissolve the metal as positive ions or to furnish negative ions which react with the metal at the interface. Either process is *oxidative* and results in the release of electrons, which flow backward through the metal, as shown in Figure 1. No metal can enter solution as positive ions or withdraw negative ions from solution, unless an equivalent reaction in the reverse direction takes place at some other point in the metal-water interface; for the solution remains electrically neutral with equivalent concentrations of positive and negative ions. This accompanying reaction is always *reductive* and results in the capture of the electrons which flow through the metal.

The corrosion of a metal is therefore an electrochemical process, such as occurs in a galvanic cell, and it is always accompanied by a

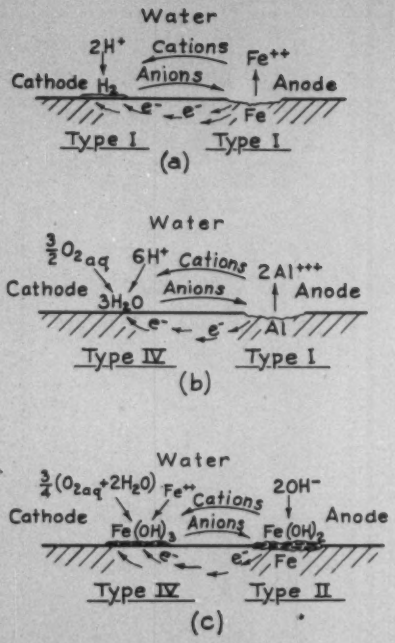

FIG. 1. Types of reactions occurring in corrosion of metals in contact with water.

flow of electric current. The rate of corrosion is equal to the current flowing. The *corrosiveness* of a water to a particular metal depends not only on its content of the ions of that metal but also upon its content of other ions and molecules capable of entering into the *oxidation-reduction* reactions.

The *oxidation* reaction by which a metal corrodes is an *anodic* reaction. The equivalent *reduction* is a *cathodic* reaction. The electric current is carried by the electrons through the metal and is carried jointly by *cations* and *anions*, which migrate in opposite directions through the solution. By convention, the direction of flow of positive electricity (cations) in the electrical circuit is from anode to cathode through the solution, which is opposite to the direction of flow of negative electricity or electrons through the metal. The voltage or potential drop through the solution is taken as positive in the direction of movement of positive ions (cations).

The reaction at each electrode is called a *half-cell* or *single-electrode* reaction. The following types of anodic reactions are common in the corrosion of metals:

Type I. $$\text{Metallic element} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \text{cations} + \text{electrons}$$

Examples: $$\underline{\text{Fe}} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \text{Fe}^{++} + 2e^-$$

$$\text{H}_2(\text{aq}) \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} 2\text{H}^+ + 2e^-$$

Type II. $$\text{Anions} + \text{metal} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \text{compound} + \text{electrons}$$

Examples: $$2\text{OH}^- + \underline{\text{Fe}} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \underline{\text{Fe(OH)}_2} + 2e^-$$

$$Cl^- + \underline{Cu} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \underline{CuCl} + e^-$$

Type III. Reductant + metal $\underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}}$ compound + cations + electrons

Examples: $H_2S(aq) + \underline{Zn} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \underline{ZnS} + 2H^+ + 2e^-$

$$HS^- + \underline{Fe} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \underline{FeS} + H^+ + 2e^-$$

The above reactions proceed from left to right at the anode. Reactions of the same type may occur at the cathode, proceeding from right to left. The following additional types of cathodic reactions, which do not involve the solid metal, are common:

Type IV. Compound $\underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}}$ oxidant + cations + electrons

Examples: $H_2O \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \frac{1}{2} O_2(aq) + 2H^+ + 2e^-$

$$\underline{Fe(OH)_3} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \frac{3}{4} O_2(aq) + \frac{3}{2} H_2O + Fe^{++} + 2e^-$$

Type V. Anions $\underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}}$ oxidant + electrons

Example: $2\,Cl^- \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} Cl_2(aq) + 2e^-$

Type VI. Compound $\underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}}$ cations + anions + electrons

Example: $\underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}}$ $Cu^{++} + Cl^{-} + e^{-}$

Thermodynamic Equilibria

The chemical reactions which occur at the electrodes of a cell involve a change in the *free energy* of the substances entering into the reactions. Willard Gibbs[1] has shown that this change in free energy is related to the e.m.f. of the cell. The relation may be stated as follows:

$$-\Delta F = \frac{96500}{4.183} n E \qquad (1)$$

in which $-\Delta F$ = the decrease in free energy of the half-cell reaction in calories per mole;
E = the reversible potential or e.m.f. of the half-cell in volts. E does not include the voltage drop through the electrolyte due to migration of ions;
n = the number of electrons transferred in the reaction (the number of faradays of electricity per mole);
96500 = the number of coulombs per faraday;
4.183 = the number of joules per calorie.

For the special case of a reaction at constant temperature and pressure and for a change of one mole for each constituent, the change in free energy is

$$\Delta F = -F_A - F_B \ldots + F_X + F_Y \qquad (2)$$

where F_A, F_B, . . . are the *partial molal free energies*[2] of the reactants

[1]Gibbs, J. W., "The Collected Works of J. Willard Gibbs," Vol. 1, p. 331 and following, Longmans, Green and Co., 1931.

[2]The designation *partial molal free energy*, symbol F, was given by Lewis and Randall (Lewis, G. N., and Randall, Merle, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., 1923) to the function called the potential μ of a constituent by Willard Gibbs. The Lewis and Randall notation has become general and will be used here.

and . . . F_X, F_Y are the *partial molal free energies* of the products of the reaction.

Gibbs also showed that the rate of change at constant temperature of the partial molal free energy with the partial pressure (or molal activity for solutes) is equal to the molal volume of the constituent as follows:

$$\left(\frac{\partial F}{\partial p}\right)_T = V_m \qquad (3)$$

This equation may be integrated at constant temperature to yield the value of F at any partial pressure p (or molal activity $\propto$) in terms of some known value of F at a reference pressure or activity. It has become customary to refer free energies to the *standard free energy*, F°_{25} (1 atm.) for gases and F°_{25} (u.a.) for solutes; where the temperature is 25°C. and the reference pressure is 1 atm. for gases and unit activity for solutes.

For gases and solutes, both of which follow the gas law, $V_m = \frac{RT}{p}$. Hence the integration of Eq. 3 defines the partial molal free energy in terms of the standard free energy as shown below. For solids and liquids, which may be assumed incompressible, both V_m and the number of molecules per unit volume are constant. Hence the partial molal free energy is constant and equal to the standard free energy. These relations are shown below:

$$\text{For gases, } F = F^\circ \text{ (1 atm.)} + RT \ln \frac{p \text{ atm.}}{1 \text{ atm.}} \qquad (4a)$$

$$\text{For solutes, } F = F^\circ \text{ (u.a.)} + RT \ln \frac{\propto \text{ moles/liter}}{1 \text{ mole/liter}} \qquad (4b)$$

$$\text{For solids and liquids, } F = F^\circ(1 \text{ atm.}) = F^\circ(\text{u.a.}) \qquad (4c)$$

In these equations F is in calories per mole, R is the gas constant, which is equal to 1.985 calories per mole per °K, and T is the absolute temperature in °K (T = 298 °K for 25°C.).

If the partial molal free energies as defined by Eq. 4 are substituted in Eq. 2, it is found that

$$\Delta F = \Delta F^\circ + RT \ln Q \tag{5}$$

where ΔF° is the algebraic sum of the standard free energies of the constituents and Q is the ratio of pressures or activities obtained from the algebraic sum of the logarithms of the pressures or activities of the constituents. For any reaction, Q is obtained by dividing the product of the pressures (or activities) of the products of the reaction by the product of the pressures (or activities) of the reactants.

The free energy of a dissolved gas has the same value, whether stated in terms of partial pressures (Eq. 4a) or molal activities (Eq. 4b). The value of F°(1 atm.) for a dissolved gas may therefore be added to values of F°(u.a.) for ionic constituents in determining ΔF° of Eq. 5, *provided* the concentration of the gas in solution is given as a partial pressure in atmospheres. The standard free energies F°(1 atm.) and F°(u.a.) for a constituent do not have the same numerical value, however. Since $pV_m = 24.45$ liter-atmospheres at 25°C., and for a gas $\frac{1}{V_m} = \propto$, it follows that

$$p = 24.45 \frac{T}{298} \propto \tag{6}$$

Integration of Eq. 3 between the limits of $p = 1$ and $p = 24.45 \frac{T}{298}$ yields the following relation between F°(1 atm.) and F°(u.a.):

$$F^\circ(1 \text{ atm.}) = F^\circ(\text{u.a.}) - RT \ln \frac{24.45 \frac{T}{298}}{1} \tag{7}$$

At 25°C., $T = 298$ and

$$F^\circ_{25}(1 \text{ atm.}) = F^\circ_{25}(\text{u.a.}) - 1890 \text{ cal./mole} \tag{7a}$$

The quantity Q in Eq. 5 has the following values for the six types of half-cell reactions commonly occurring in metallic corrosion:

Type I. $Q = (\propto_{M^+})^{n_{M^+}}$ or $\frac{(\propto_{H^+})^2}{p_{H_2\,(gas)}}$ for hydrogen

Type II. $Q = \frac{1}{(\propto_{A^-})^{n_{A^-}}}$

Type III. $Q = \frac{(\propto_{M^+})^{n_{M^+}}}{\propto_{Red}}$ (8)

Type IV. $Q = \propto_{Oxi}(\propto_{M^+})^{n_{M^+}}$

Type V. $Q = \frac{\propto_{Oxi}}{(\propto_{A^-})^{n_{A^-}}}$

Type VI. $Q = (\propto_{M^+})^{n_{M^+}}(\propto_{A^-})^{n_{A^-}}$

where $\propto_{M^+}$, $\propto_{A^-}$, $\propto_{Red}$, $\propto_{Oxi}$ are the activities of the metallic ion, anion, reductant and oxidant, respectively, and n_{M^+}, n_{A^-} are the numbers of ions taking part in the reaction.

From Eq. 1, the *standard oxidation potential* corresponding to the standard free energy change ΔF° at any temperature T is:

$$E^\circ = -\frac{4.183}{96500\,n}\Delta F^\circ \qquad (9)$$

Hence, from Eqs. 1, 5 and 9, the *oxidation potential* for any half-cell reaction is:

$$E = E^\circ - \frac{4.183\,RT}{96500\,n}\ln Q \qquad (10)$$

For a temperature of 25°C., the *oxidation potential* is given by

$$E_{25} = E^\circ_{25} - 0.05914\log Q^{\frac{1}{n}} \qquad (10a)$$

in which E°_{25} is the standard oxidation potential at 25°C. corresponding to ΔF°_{25}.

The reversible potential for a whole cell is the difference between

the oxidation potentials at the two electrodes (or the sum of the oxidation and reduction potentials) as follows :

$$\Delta E_{25} = \Delta E^{\circ}_{25} - 0.05914 \log \frac{Q_1^{\frac{1}{n_1}}}{Q_2^{\frac{1}{n_2}}} \qquad (11)$$

in which ΔE°_{25} is the difference between the standard oxidation potentials, the subscripts 1 and 2 refer to the oxidation reactions at the anode and cathode respectively, and n_1 and n_2 are the number of electrons transferred. At equilibrium, there is no flow of electricity through the cell and $\Delta E = 0$. Hence, at equilibrium,

$$\Delta E^{\circ}_{25} = 0.05914 \log K \qquad (12)$$

where the equilibrium constant K is the value of

$\frac{Q_1^{\frac{1}{n_1}}}{Q_2^{\frac{1}{n_2}}}$ at equilibrium.

Criterion for Corrosion

It follows from Eqs. 11 and 12 that any single metal which is in contact with an aqueous solution at 25°C. may corrode, *if*

$$\frac{Q_1^{\frac{1}{n_1}}}{Q_2^{\frac{1}{n_2}}} \text{ is less than } 10^{\frac{\Delta E^{\circ}_{25}}{0.05914}} \qquad (13)$$

where the subscript 1 refers to the anodic reaction and the subscript 2 refers to any single electrode reaction which the composition of the water will permit at the cathode. The most important single factor in this criterion for corrosion is the magnitude of ΔE°, the difference in the standard oxidation potentials of the two half-cell reactions. For example, if the

value of ΔE°_{25} is only 0.1 volt, the value of the ratio $\frac{Q_1^{\frac{1}{n_1}}}{Q_2^{\frac{1}{n_2}}}$ must exceed 49 to stop corrosion; and, if the value of ΔE°_{25} is 0.2 volts, $\frac{Q_1^{\frac{1}{n_1}}}{Q_2^{\frac{1}{n_2}}}$ must exceed 2400.

The flow of electricity always tends to start at the highest potential and the first half-cell reactions which will take place are those involving the greatest magnitude of ΔE. If the magnitude of $\frac{Q_1^{\frac{1}{n_1}}}{Q_2^{\frac{1}{n_2}}}$ is permitted to increase sufficiently with the continuance of the reaction, ΔE is reduced in value and other reactions, involving lower magnitudes of ΔE, will come successively into play until the cell is discharged.

In order to determine what reaction will take place at the anode for a particular metal and a particular water, it is necessary to examine all possible anodic reactions in pairs by means of the above criterion, Eq. 13, to determine which is the most anodic. Similarly, it is necessary to examine all possible cathodic reactions to determine which is the most cathodic. The effects of the various substances in the water—that is, the *corrosiveness* of the water—may thus be determined. The method of attack is illustrated at the end of this paper by some simple examples.

If a second metal or electrode having a higher oxidation potential than the first metal is in contact with both the solution and the first metal, the anodic reaction involving the oxidation of the first metal will not take place. Corrosion of the first metal is thus pre-

vented by *cathodic protection;* that is, the first metal is made to function only as a cathode.

Standard Oxidation Potentials

In order to apply the criterion for corrosion, it is necessary to know the standard oxidation potentials for all conceivable half-cell reactions.

It has not been possible to measure absolute values of half-cell potentials. For convenience, the *hydrogen electrode* is arbitrarily chosen as a reference electrode, and the half-cell potential is set arbitrarily at zero *at any temperature* when the pressure of hydrogen gas in contact with the solution is 1 atm. and the hydrogen ions are at unit activity (pH = 0.0). The reaction for this half-cell may be represented as follows:

$$H_2(\text{gas})(1\text{atm.}) \rightleftharpoons H_2(\text{aq}) \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} 2H^+(\text{u.a.}) + 2e^- \qquad (14)$$

$$E^\circ = 0.0$$

The electrode reaction is between the dissolved hydrogen and the hydrogen ions. Since the free energy of H_2(gas) at 1 atm. is arbitrarily defined as zero, the arbitrary zero potential for this electrode conforms with the zero value assigned to the free energy of hydrogen ions at unit activity and *any temperature*.

The single electrode potential of any half-cell when referred to the hydrogen electrode is, by definition, therefore, the total reversible e.m.f. of a cell with hydrogen as one of the electrodes. Values of *standard oxidation potentials* at 25°C. for many of the common half-cell reactions occurring in the corrosion of metals are shown in Table 1. Some of these potentials were taken from a table presented by Latimer.[3] Most of them, however, were computed by the author by means of Eq. 9 from the standard free energies of the constituents, as given by Latimer[3] and others. In reactions involving dissolved gases, the subscript aq is used with the symbol for the gas and the

[3]Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., 1938.

standard free energy, F^*_{25} (u.a.), of the dissolved gas, computed from its solubility, is used for the evaluation of E^*_{25}. The trained chemist will recognize that some of the reactions listed in Table 1 do not take place under ordinary conditions. If an anodic reaction does not take place, it is because there is always another reaction which is more anodic; and if a cathodic reaction does not occur, it is because there is always another reaction which is more cathodic. The reactions which may occur may readily be determined by applying the criterion for corrosion. The reactions in Table 1 are therefore to be considered as conceivable rather than actual.

TABLE 1.—STANDARD OXIDATION POTENTIALS AT 25°C. OF SOME HALF-CELL REACTIONS TO BE CONSIDERED IN CORROSION OF METALS IN WATER

	Oxidation reaction	E^*_{25}, volts
1.	$CO_3^{--} + \underline{Ca} \longrightarrow \underline{CaCO_3} + 2e^-$	+3.12
2.	$2\ OH^- + \underline{Ca} \longrightarrow \underline{Ca(OH)_2} + 2e^-$	+3.02
3.	$\underline{K} \longrightarrow K^+ + e^-$	+2.922
4.	$\underline{Ca} \longrightarrow Ca^{++} + 2e^-$	+2.87
5.	$\underline{Na} \longrightarrow Na^+ + e^-$	+2.712
6.	$2\ OH^- + \underline{Mg} \longrightarrow \underline{Mg(OH)_2} + 2e^-$	+2.67
7.	$CO_3^{--} + \underline{Mg} \longrightarrow \underline{MgCO_3} + 2e^-$	+2.60
8.	$4\ OH^- + \underline{Al} \longrightarrow H_2Al\ O_3^- + H_2O + 3e^-$	+2.35
9.	$\underline{Mg} \longrightarrow Mg^{++} + 2e^-$	+2.34
10.	$3\ OH^- + \underline{Al} \longrightarrow \underline{Al(OH)_3} + 3e^-$	+2.318
11.	$6\ OH^- + \underline{Si} \longrightarrow SiO_3^{--} + 3\ H_2O + 4e^-$	+1.73
12.	$5\ OH^- + \underline{Si} \longrightarrow HSiO_3^- + 2\ H_2O + 4e^-$	+1.70
13.	$4\ OH^- + \underline{Si} \longrightarrow \underline{H_2SiO_3} + H_2O + 4e^-$	+1.67
14.	$\underline{Al} \longrightarrow Al^{+++} + 3e^-$	+1.67
15.	$6\ OH^- + Sn^{++} \longrightarrow Sn(OH)_6^{--} + 2e^-$	+1.60
16.	$2\ OH^- + \underline{Mn} \longrightarrow \underline{Mn(OH)_2} + 2e^-$	+1.47
17.	$S^{--} + \underline{Zn} \longrightarrow \underline{ZnS} + 2e^-$	+1.44
18.	$2\ OH^- + \underline{Zn} \longrightarrow \underline{Zn(OH)_2} + 2e^-$	+1.42
19.	$CO_3^{--} + \underline{Mn} \longrightarrow \underline{MnCO_3} + 2e^-$	+1.35
20.	$3\ OH^- + \underline{Cr} \longrightarrow \underline{Cr(OH)_3} + 3e^-$	+1.30
21.	$S^{--} + \underline{Cd} \longrightarrow \underline{CdS} + 2e^-$	+1.23
22.	$4\ OH^- + \underline{Zn} \longrightarrow ZnO_2^{--} + 2\ H_2O + 2e^-$	+1.216
23.	$4\ OH^- + \underline{Cr} \longrightarrow CrO_2^{-} + 2\ H_2O + 3e^-$	+1.2
24.	$3\ OH^- + \underline{Mn} \longrightarrow \underline{Mn(OH)_3} + 3e^-$	+1.12
25.	$S^{--} + \underline{Ni} \longrightarrow \underline{NiS}(\gamma) + 2e^-$	+1.07
26.	$CO_3^{--} + \underline{Zn} \longrightarrow \underline{ZnCO_3} + 2e^-$	+1.07
27.	$\underline{Mn} \longrightarrow Mn^{++} + 2e^-$	+1.05

TABLE 1 (*continued*)

	Oxidation reaction	E°_{25}, volts
28.	$4\ NH_{3_{aq}} + \underline{Zn} \longrightarrow Zn(NH_3)_4^{++} + 2e^-$	+1.03
29.	$S^{--} + \underline{Ni} \longrightarrow \underline{NiS}(\beta) + 2e^-$	+1.02
30.	$HS^- + \underline{Zn} \longrightarrow \underline{ZnS} + H^+ + 2e^-$	+1.00
31.	$S^{--} + \underline{Fe} \longrightarrow \underline{FeS} + 2e^-$	+1.00
32.	$S^{--} + \underline{Pb} \longrightarrow \underline{PbS} + 2e^-$	+0.98
33.	$3\ OH^- + H_2O + HSnO_2^- \longrightarrow Sn(OH)_6^{--} + 2e^-$	+0.96
34.	$S^{--} + \underline{2\ Cu} \longrightarrow \underline{Cu_2S} + 2e^-$	+0.95
35.	$2\ OH^- + \underline{Sn} \longrightarrow \underline{Sn(OH)_2} + 2e^-$	+0.883
36.	$2\ OH^- + \underline{Fe} \longrightarrow \underline{Fe(OH)_2} + 2e^-$	+0.877
37.	$OH^- + HCO_3^- + \underline{Fe} \longrightarrow \underline{FeCO_3} + H_2O + 2e^-$	+0.865
38.	$S^{--} + \underline{Ni} \longrightarrow \underline{NiS}(\alpha) + 2e^-$	+0.86
39.	$\underline{Cr} \longrightarrow Cr^{++} + 2e^-$	+0.855
40.	$S^{--} + \underline{Pt} \longrightarrow \underline{PtS} + 2e^-$	+9.83
41.	$2\ OH^- + H_{2_{aq}} \longrightarrow 2H_2O + 2e^-$	+0.828
42.	$4\ OH^- + \underline{Sn} \longrightarrow \underline{Sn(OH)_4} + 4e^-$	+0.82
43.	$2\ OH^- + \underline{Cd} \longrightarrow \underline{Cd(OH)_2} + 2e^-$	+0.815
44.	$CO_3^{--} + \underline{Cd} \longrightarrow \underline{CdCO_3} + 2e^-$	+0.80
45.	$H_2S_{aq} + \underline{Zn} \longrightarrow \underline{ZnS} + 2H^+ + 2e^-$	+0.794
46.	$3\ OH^- + \underline{Sn} \longrightarrow HSnO_2^- + H_2O + 2e^-$	+0.79
47.	$HS^- + \underline{Cd} \longrightarrow \underline{CdS} + H^+ + 2e^-$	+0.78
48.	$3\ OH^- + \underline{Fe} \longrightarrow \underline{Fe(OH)_3} + 3e^-$	+0.775
49.	$\underline{Zn} \longrightarrow Zn^{++} + 2e^-$	+0.762
50.	$S^{--} + \underline{Cu} \longrightarrow \underline{CuS} + 2e^-$	+0.76
51.	$CO_3^- + \underline{Fe} \longrightarrow \underline{FeCO_3} + 2e^-$	+0.755
52.	$2\ Cl^- + \underline{Cr} \longrightarrow CrCl_2^- + 3e^-$	+0.74
53.	$4\ OH^- + \underline{Mn} \longrightarrow \underline{MnO_2} + 2\ H_2O + 4e^-$	+0.715
54.	$Cr \longrightarrow \underline{Cr}^{+++} + 3e^-$	+0.71
55.	$S^{--} + \underline{2\ Ag} \longrightarrow \underline{Ag_2S} + 2e^-$	+0.71
56.	$8\ OH^- + \underline{Cr} \longrightarrow CrO_4^{--} + 4\ H_2O + 6e^-$	+0.705
57.	$S^{--} + Hg \longrightarrow HgS + 2e^-$	+0.70
58.	$2\ OH^- + \underline{Ni} \longrightarrow \underline{Ni(OH)_2} + 2e^-$	+0.66
59.	$7\ OH^- + \underline{Cr} \longrightarrow HCrO_4^- + 3\ H_2O + 6e^-$	+0.63
60.	$HS^- + \underline{Ni} \longrightarrow \underline{NiS}(\gamma) + H^+ + 2e^-$	+0.622
61.	$4\ NH_{3_{aq}} + \underline{Cd} \longrightarrow Cd(NH_3)_4^{++} + 2e^-$	+0.597
62.	$2\ OH^- + \underline{Pb} \longrightarrow \underline{Pb(OH)_2} + 2e^-$	+0.585
63.	$H_2S + \underline{Cd} \longrightarrow \underline{CdS} + 2H^+ + 2e^-$	+0.575
64.	$HS^- + \underline{Ni} \longrightarrow \underline{NiS}(\beta) + H^+ + 2e^-$	+0.573
65.	$OH^- + \underline{Fe(OH)_2} \longrightarrow \underline{Fe(OH)_3} + e^-$	+0.566
66.	$HS^- + \underline{Fe} \longrightarrow \underline{FeS} + H^+ + 2e^-$	+0.56
67.	$3\ OH^- + \underline{Pb} \longrightarrow HPbO_2^- + H_2O + 2e^-$	+0.54

TABLE 1 (*continued*)

	Oxidation reaction	E°_{25}, volts
68.	$S^{--} \longrightarrow \underline{S} + 2e^-$	+0.508
69.	$CO_3^{--} + \underline{Pb} \longrightarrow \underline{PbCO_3} + 2e^-$	+0.506
70.	$HS^- + \underline{2\,Cu} \longrightarrow \underline{Cu_2S} + H^+ + 2e^-$	+0.502
71.	$6\,NH_{3_{aq}} + \underline{Ni} \longrightarrow Ni(NH_3)_6^{++} + 2e^-$	+0.48
72.	$OH^- + HS^- \longrightarrow \underline{S} + H_2O + 2e^-$	+0.478
73.	$CO_3^{--} + \underline{Ni} \longrightarrow \underline{NiCO_3} + 2e^-$	+0.45
74.	$\underline{Fe} \longrightarrow Fe^{++} + 2e^-$	+0.440
75.	$H_2S_{aq} + \underline{Ni} \longrightarrow \underline{NiS}(\gamma) + 2H^+ + 2e^-$	+0.417
76.	$HS^- + \underline{Ni} \longrightarrow \underline{NiS}(\alpha) + H^+ + 2e^-$	+0.411
77.	$\underline{Cd} \longrightarrow Cd^{++} + 2e^-$	+0.402
78.	$OH^- + \underline{Mn(OH)_2} \longrightarrow \underline{Mn(OH)_3} + e^-$	+0.40
79.	$H_2S_{aq} + \underline{Ni} \longrightarrow \underline{NiS}(\beta) + 2H^+ + 2e^-$	+0.368
80.	$2\,OH^- + \underline{2\,Cu} \longrightarrow \underline{Cu_2O} + H_2O + 2e^-$	+0.361
81.	$SO_4^- + \underline{Pb} \longrightarrow \underline{PbSO_4} + 2e^-$	+0.355
82.	$H_2S_{aq} + \underline{2\,Cu} \longrightarrow \underline{Cu_2S} + 2H^+ + 2e^-$	+0.296
83.	$8\,OH^- + \underline{Mn} \longrightarrow MnO_4^{--} + 4\,H_2O + 6e^-$	+0.283
84.	$2\,Cl^- + \underline{Pb} \longrightarrow \underline{PbCl_2} + 2e^-$	+0.268
85.	$\underline{Ni} \longrightarrow Ni^{++} + 2e^-$	+0.250
86.	$2\,OH^- + \underline{Cu} \longrightarrow \underline{Cu\,((OH)_2} + 2e^-$	+0.224
87.	$H_2S_{aq} + \underline{Ni} \longrightarrow \underline{NiS}(\alpha) + 2H^+ + 2e^-$	+0.205
88.	$8\,OH^- + \underline{Mn} \longrightarrow MnO_4^- + 4\,H_2O + 7e^-$	+0.165
89.	$4\,OH^- + \underline{Pb} \longrightarrow \underline{PbO_2} + 2\,H_2O + 4e^-$	+0.163
90.	$4\,OH^- + \underline{Cu} \longrightarrow CuO_2^{--} + 2\,H_2O + 2e^-$	+0.138
91.	$\underline{Sn} \longrightarrow Sn^{++} + 2e^-$	+0.136
92.	$\underline{Pb} \longrightarrow Pb^{++} + 2e^-$	+0.126
93.	$5\,OH^- + \underline{Cr(OH)_3} \longrightarrow CrO_4^{--} + 4\,H_2O + 3e^+$	+0.12
94.	$3\,OH^- + \underline{Cu} \longrightarrow HCuO_2^- + H_2O + 2e^-$	+0.114
95.	$H_2S_{aq} + \underline{Cu} \longrightarrow \underline{CuS} + 2H^+ + 2e^-$	+0.113
96.	$2\,NH_{3_{aq}} + \underline{Cu} \longrightarrow Cu(NH_3)_2^+ + e^-$	+0.11
97.	$HS^- \longrightarrow \underline{S} + H^+ + 2e^-$	+0.064
98.	$4\,NH_{3_{aq}} + \underline{Cu} \longrightarrow Cu(NH_3)_4^{++} + 2e^-$	+0.05
99.	$\underline{Fe} \longrightarrow Fe^{+++} + 3e^-$	+0.036
100.	$H_{2_{gas}}$ (1 atm.) $\longrightarrow 2H^+$(u.a.) $+ 2e^-$	+0.000
101.	$CO_3^{--} + \underline{Cu} \longrightarrow \underline{CuCO_3} + 2e^-$	−0.053
102.	$2\,OH^- + \underline{Hg} \longrightarrow \underline{HgO}(r) + H_2O + 2e^-$	−0.0984
103.	$2\,OH^- + \underline{Pd} \longrightarrow \underline{Pd(OH)_2} + 2e^-$	−0.1
104.	$2\,HCO_3^- + \underline{Ca} \longrightarrow \underline{CaCO_3} + 2H^+ + 4e^-$	−0.114

TABLE 1 (*continued*)

	Oxidation reaction	E°_{25}, volts
105.	$2\ OH^- + 2\ Hg \longrightarrow \underline{Hg_2O} + H_2O + 2e^-$	—0.123
106.	$Cl^- + \underline{Cu} \longrightarrow \underline{CuCl} + e^-$	—0.124
107.	$H_2S_{aq} \longrightarrow \underline{S} + 2H^+ + 2e^-$	—0.141
108.	$4\ H_2O + Sn^{++} \longrightarrow \underline{Sn(OH)_4} + 4H^+ + 2e^-$	—0.154
109.	$2\ OH^- + \underline{Pt} \longrightarrow \underline{Pt(OH)_2} + 2e^-$	—0.16
110.	$2\ Cl^- + \underline{Cu} \longrightarrow \underline{CuCl_2^-} + e^-$	—0.19
111.	$Cl^- + \underline{Ag} \longrightarrow \underline{AgCl} + e^-$	—0.222
112.	$2\ Cl^- + Hg \longrightarrow \underline{Hg_2Cl_2} + 2e^-$	—0.267
113.	$3\ H_2O + Cr^{++} \longrightarrow \underline{CrOH_3} + 3H^+ + e^-$	—0.291
114.	$CO_3^{--} + 2\ Hg \longrightarrow \underline{Hg_2CO_3} + 2e^-$	—0.32
115.	$2\ OH^- + \underline{2\ Ag} \longrightarrow \underline{Ag_2O} + H_2O + 2e^-$	—0.344
116.	$\underline{Cu} \longrightarrow Cu^{++} + 2e^-$	—0.345
117.	$2\ HCO_3^- + \underline{Mg} \longrightarrow \underline{MgCO_3} + 2H^+ + 4e^-$	—0.372
118.	$2\ NH_{3_{aq}} + Ag \longrightarrow Ag(NH_3)_2^+ + e^-$	—0.373
119.	$4\ Cl^- + Hg \longrightarrow HgCl_4^{--} + 2e^-$	—0.38
120.	$2\ OH^- \longrightarrow \frac{1}{2}\ O_{2_{aq}} + H_2O + 2e^-$	—0.444
121.	$CO_3^{--} + \underline{2\ Ag} \longrightarrow \underline{Ag_2CO_3} + 2e^-$	—0.47
122.	$2\ OH^- + \underline{Ni(OH)_2} \longrightarrow \underline{NiO_2} + 2\ H_2O + 2e^-$	—0.49
123.	$OH^- + HSiO_3^- \longrightarrow \underline{H_2SiO_3} + \frac{1}{2}\ O_{2_{aq}} + 2e^-$	—0.50
124.	$\underline{Cu} \longrightarrow Cu^+ + e^-$	—0.552
125.	$Cl^- + 2\ H^+ + CuO_2^{--} \longrightarrow OCl^- + H_2O + Cu^{++} + 2e^-$	—0.535
126.	$MnO_4^{--} \longrightarrow MnO_4^- + e^-$	—0.54
127.	$\underline{CuCl} \longrightarrow Cu^{++} + Cl^- + e^-$	—0.566
128.	$4\ OH^- + \underline{MnO_2} \longrightarrow MnO_4^- + 2\ H_2O + 3e^-$	—0.57
129.	$2\ OH^- + \underline{Ag_2O} \longrightarrow \underline{2\ AgO} + H_2O + 2e^-$	—0.57
130.	$4\ OH^- + \underline{MnO_2} \longrightarrow MnO_4^{--} + 2\ H_2O + 2e^-$	—0.58
131.	$SO_4^{--} + 2\ Hg \longrightarrow \underline{Hg_2SO_4} + 2e^-$	—0.615
132.	$4\ Cl^- + \underline{Pd} \longrightarrow PdCl_4^{--} + 2e^-$	—0.64
133.	$SO_4^{--} + \underline{2\ Ag} \longrightarrow \underline{Ag_2SO_4} + 2e^-$	—0.653
134.	$2\ CO_3^{--} + H_2O \longrightarrow 2\ HCO_3^- + \frac{1}{2}\ O_{2_{aq}} + 2e^-$	—0.66
135.	$ZnO_2^{--} \longrightarrow O_{2_{aq}} + Zn^{++} + 4e^-$	—0.67
136.	$CuO_2^{--} \longrightarrow O_{2_{aq}} + Cu^{++} + 4e^-$	—0.685
137.	$2\ H_2O + Cu^+ \longrightarrow \underline{Cu(OH)_2} + 2H^+ + e^-$	—0.687
138.	$4\ Cl^- + \underline{Pt} \longrightarrow PtCl_4^{--} + 2e^-$	—0.73
139.	$2\ OH^- + \underline{2\ AgO} \longrightarrow \underline{Ag_2O_3} + H_2O + 2e^-$	—0.74
140.	$\underline{Cu_2O} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + 2\ Cu^{++} + 4e^-$	—0.75
141.	$H_2O_{2_{aq}} \longrightarrow O_{2_{aq}} + 2H^{++} + 2e^-$	—0.768

TABLE 1 (*continued*)

	Oxidation reaction	E°_{25}, volts
142.	$Fe^{++} \longrightarrow Fe^{+++} + e^-$	—0.771
143.	$2\ OH^- + \underline{CuCl} \longrightarrow OCl^- + H_2O + Cu^{++} + 3e^-$	—0.777
144.	$CO_3^{--} + H_2O \longrightarrow H_2CO_3 + \frac{1}{2}\ O_{2_{aq}} + 2e^-$	—0.779
145.	$MnO_4^{--} \longrightarrow 2\ O_{2_{aq}} + Mn^{++} + 4e^-$	—0.785
146.	$2\ Hg \longrightarrow Hg_2^{++} + 2e^-$	—0.7986
147.	$\underline{Ag} \longrightarrow Ag^+ + e^-$	—0.7995
148.	$4\ OH^- + CuCl_2^- \longrightarrow 2\ OCl^- + 2\ H_2O + Cu^{++} + 5e^-$	—0.805
149.	$\underline{Pd} \longrightarrow Pd^{++} + 2e^-$	—0.83
150.	$\underline{Ni(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Ni^{++} + H_2O + 2e^-$	—0.852
151.	$Hg \longrightarrow Hg^{++} + 2e^-$	—0.854
152.	$\underline{Cd(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Cd^{++} + H_2O + 2e^-$	—0.855
153.	$HPbO_2^- \longrightarrow O_{2_{aq}} + Pb^{++} + H^+ + 4e^-$	—0.857
154.	$Cl^- + H^+ + \underline{Cu_2O} \longrightarrow HOCl + 2\ Cu^{++} + 4e^-$	—0.86
155.	$\underline{Mn(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Mn^{++} + H_2O + 2e^-$	—0.862
156.	$MnO_4^- \longrightarrow 2\ O_{2_{aq}} + Mn^{++} + 3e^-$	—0.866
157.	$Cl^- + H^+ + HPbO_2^- \longrightarrow OCl + H_2O + Pb^{++} + 2e^-$	—0.877
158.	$2\ OH^- + Cl^- \longrightarrow OCl^- + H_2O + 2e^-$	—0.878
159.	$HCuO_2^- \longrightarrow O_{2_{aq}} + Cu^{++} + H^+ + 4e^-$	—0.88
160.	$\underline{Fe(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Fe^{++} + H_2O + 2e^-$	—0.882
161.	$2\ Cl^- + 2\ H^+ + ZnO_2^{--} \longrightarrow 2\ HOCl + Zn^{++} + 4e^-$	—0.892
162.	$\underline{Pb(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Pb^{++} + H_2O + 2e^-$	—0.904
163.	$2\ Cl^- + 2H^+ + CuO_2^- \longrightarrow 2\ HOCl + Cu^{++} + 4e^-$	—0.907
164.	$OH^- + \underline{CuCl} \longrightarrow HOCl + Cu^{++} + 3e^-$	—0.91
165.	$Cl^- + H^+\ HCuO_2^- \longrightarrow OCl^- + H_2O + Cu^{++} + 2e^-$	—0.926
166.	$\underline{Zn(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Zn^{++} + H_2O + 2e^-$	—0.927
167.	$4\ OH^- + \underline{PbCl_2} \longrightarrow 2\ OCl^- + 2\ H_2O + Pb^{++} + 4e^-$	—0.95
168.	$H_2AlO_3^- \longrightarrow O_{2_{aq}} + Al^{+++} + H_2O + 4e^-$	—0.952
169.	$\underline{Pb_3O_4} \longrightarrow 2\ O_{2_{aq}} + 3\ Pb^{++} + 6e^-$	—0.96
170.	$Cl^- + \underline{Cu_2O} \longrightarrow OCl^-\ 2\ Cu^{++} + 4e^-$	—0.964
171.	$2\ OH^- + CuCl_2^- \longrightarrow 2\ HOCl + Cu^{++} + 5e^-$	—0.965
172.	$HSnO_2^- \longrightarrow O_{2_{aq}} + Sn^{++} + H^+ + 4e^-$	—0.977
173.	$2\ HCO_3^- + \underline{Mn} \longrightarrow \underline{MnCO_3} + 2\ H^+ + 4e^-$	—1.00
174.	$\underline{Cu(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Cu^{++} + H_2O + 2e^-$	—1.01

TABLE 1 (*continued*)

	Oxidation reaction	E°_{25}, volts
175.	$Cl^- + \underline{Ca(OH)_2} \longrightarrow OCl^- + H_2O + Ca^{++} + 2e^-$	—1.03
176.	$\underline{Cr(OH)_3} \longrightarrow \frac{3}{4}\ O_2 + Cr^{+++} + \frac{3}{2}\ H_2O + 3e^-$	—1.04
177.	$3\ H_2O + Fe^{++} \longrightarrow \underline{Fe(OH)_3} + 3H^+ + e^-$	—1.044
178.	$2\ Cl^- + H^+ + HPbO_2^- \longrightarrow 2\ HOCl + Pb^{++} + 4e^-$	—1.08
179.	$HCO_3^- + H_2O \longrightarrow \frac{1}{2}\ O_{2_{aq}} + H_2CO_3 + H^+ + 2e^-$	—1.083
180.	$\underline{PbO_2} \longrightarrow O_{2_{aq}} + Pb^{++} + 2e^-$	—1.086
181.	$\underline{Al(OH)_3} \longrightarrow \frac{3}{4}\ O_{2_{aq}} + Al^{+++} + \frac{3}{2}\ H_2O + 3e^-$	—1.09
182.	$2\ Cl + H^+ + HCuO_2^- \longrightarrow 2\ HOCl + Cu^{++} + 4e^-$	—1.103
183.	$Cl^- + \underline{Mg(OH)_2} \longrightarrow OCl^- + H_2O + Mg^{++} + 2e^-$	—1.105
184.	$2\ Cl^- + ZnO_2^{--} \longrightarrow 2\ OCl^- + Zn^{++} + 4e^-$	—1.108
185.	$Cl^- + H^+ + HSnO_2^- \longrightarrow OCl^- + H_2O + Sn^{++} + 2e^-$	—1.12
186.	$2\ OH^- + \underline{PbCl_2} \longrightarrow 2\ HOCl + Pb^{++} + 4e^-$	—1.15
187.	$2\ HCO_3^- + \underline{Zn} \longrightarrow \underline{ZnCO_3} + 2\ H^+ + 4e^-$	—1.151
188.	$2\ Cl^- + \underline{Ca(OH)_2} \longrightarrow 2\ HOCl + Ca^{++} + 4e^-$	—1.155
189.	$\underline{Fe(OH)_3} \longrightarrow \frac{3}{4}\ O_{2_{aq}} + Fe^{+++} + \frac{3}{2}\ H_2O + 3e^-$	—1.18
190.	$2\ Cl^- + \underline{Mg(OH)_2} \longrightarrow 2\ HOCl + Mg^{++} + 4e^-$	—1.19
191.	$\underline{Sn(OH)_2} \longrightarrow \frac{1}{2}\ O_{2_{aq}} + Sn^{++} + H_2O + 2e^-$	—1.193
192.	$\underline{Pt} \longrightarrow Pt^{++} + 2e^-$	—1.2
193.	$2\ Cl^- + H^+ + HSnO_2^- \longrightarrow 2\ HOCl + Sn^{++} + 4e^-$	—1.20
194.	$4\ Cl^- + 4H^+ + MnO_4^{--} \longrightarrow 4\ HOCl + Mn^{++} + 4e^-$	—1.23
195.	$3\ H_2O + Mn^{++} \longrightarrow \underline{Mn(OH)_3} + 3H^+ e^-$	—1.244
196.	$\underline{CrO_2} \longrightarrow O_{2_{aq}} + Cr^{++} + 3e^-$	—1.265
197.	$\underline{MnO_2} \longrightarrow O_{2_{aq}} + Mn^{++} + 2e^-$	—1.265
198.	$H_2O \longrightarrow \frac{1}{2}\ O_{2_{aq}} + 2H^+ + 2e^-$	—1.273
199.	$2\ HCO_3^- + \underline{Cd} \longrightarrow \underline{CdCO_3} + 2H^+ + 4e^-$	—1.276
200.	$H_2O \longrightarrow \frac{1}{3}\ O_{3_{aq}} + 2H^+ + 2e^-$	—1.28
201.	$2\ H_2O + Mn^{++} \longrightarrow \underline{MnO_2} + 4H^+ + 2e^-$	—1.28
202.	$3\ Cl^- + H^+ + H_2AlO_3^- \longrightarrow 3\ HOCl + Al^{+++} + 6e^-$	—1.285
203.	$2\ Cl^- + \underline{Ni(OH)_2} \longrightarrow 2\ HOCl + Ni^{++} + 4e^-$	—1.286
204.	$2\ Cl^- + \underline{Cd(OH)_2} \longrightarrow 2\ HOCl + Cd^{++} + 4e^-$	—1.286
205.	$2\ Cl^- + \underline{Mn(OH)_2} \longrightarrow 2\ HOCl + Mn^{++} + 4e^-$	—1.29
206.	$Cl^- + \underline{Ni\ (OH)_2} \longrightarrow OCl^- + H_2O + Ni^{++} + 2e^-$	—1.29
207.	$\underline{Mn(OH)_3} \longrightarrow \frac{3}{4}\ O_{2_{aq}} + Mn^{++} + \frac{3}{2}\ H_2O + 2e^-$	—1.29
208.	$Cl^- + \underline{Cd(OH)_2} \longrightarrow OCl^- + H_2O + Cd^{++} + 2e^-$	—1.294
209.	$2\ HCO_3^- + \underline{Fe} \longrightarrow \underline{FeCO_3} + 2H^+ + 4e^-$	—1.30

TABLE 1 (*continued*)

	Oxidation reaction	E°_{25}, volts
210.	$2\ Cl^- + \underline{Fe(OH)_2} \longrightarrow 2\ HOCl + Fe^{++} + 4e^-$	—1.30
211.	$Cl^- + \underline{Mn(OH)_2} \longrightarrow OCl^- + H_2O + Mn^{++} + 2e^-$	—1.30
212.	$2\ Cl^- + \underline{Pb(OH)_2} \longrightarrow 2\ HOCl + Pb^{++} + 4e^-$	—1.31
213.	$Cl^- + \underline{Fe(OH)_2} \longrightarrow OCl^- + H_2O + Fe^{++} + 2e^-$	—1.32
214.	$2\ Cl^- + \underline{Zn(OH)_2} \longrightarrow 2\ HOCl + Zn^{++} + 4e^-$	—1.32
215.	$Cl^- + \underline{Pb(OH)_2} \longrightarrow OCl^- + H_2O + Pb^{++} + 2e^-$	—1.34
216.	$2\ Cl^-$ (u.a.) $\longrightarrow Cl_{2\ gas}$ (1 atm.) $+ 2e^-$	—1.358
217.	$Cl^- + \underline{Zn(OH)_2} \longrightarrow OCl^- + H_2O + Zn^{++} + 2e^-$	—1.36
218.	$2\ Cl^- + \underline{Cu(OH)_2} \longrightarrow 2\ HOCl + Cu^{++} + 4e^-$	—1.365
219.	$3\ Cl^- + \underline{Cr(OH)_3} \longrightarrow 3\ HOCl + Cr^{+++} + 6e^-$	—1.38
220.	$\underline{Fe(OH)_3} \longrightarrow {}^3/_4\ O_{2\ aq} + Fe^{++} + {}^3/_2\ H_2O + 2e^-$	—1.386
221.	$2\ Cl^- + H_2AlO_3^- \longrightarrow 2\ OCl^- + H_2O + Al^{+++} + 4e^-$	—1.39
222.	$3\ Cl^- + \underline{Al(OH)_3} \longrightarrow 3\ HOCl + Al^{+++} + 6e^-$	—1.40
223.	$\underline{Au} \longrightarrow Au^{+++} + 3e^-$	—1.42
224.	$2\ HCO_3^- + \underline{Pb} \longrightarrow \underline{PbCO_3} + 2H^+ + 4e^-$	—1.42
225.	$Cl^- + \underline{Cu(OH)_2} \longrightarrow OCl^- + H_2O + Cu^{++} + 2e^-$	—1.45
226.	$3\ Cl^- + \underline{Fe(OH)_3} \longrightarrow 3\ HOCl + Fe^{+++} + 6e^-$	—1.45
227.	$2\ Cl^- + \underline{Sn(OH)_2} \longrightarrow 2\ HOCl + Sn^{++} + 4e^-$	—1.45
228.	$2\ HCO_3^- + \underline{Ni} \longrightarrow \underline{NiCO_3} + 2H^+ + 4e^-$	—1.45
229.	$2\ H_2O + Pb^{++} \longrightarrow \underline{PbO_2} + 4H^+ + 2e^-$	—1.456
230.	$4\ Cl^- + 4H^+ + MnO_4^- \longrightarrow 4\ HOCl + Mn^{++} + 3e^-$	—1.46
231.	$Sn(OH)_6^{--} \longrightarrow {}^3/_2\ O_{2\ aq} + Sn^{++} + 3\ H_2O + 4e^-$	—1.47
232.	$3\ Cl^- + \underline{2\ Cr(OH)_3} \longrightarrow 3\ OCl^- + 3\ H_2O + 2\ Cr^{++} + 6e^-$	—1.47
233.	$Cl^- + H_2O \longrightarrow HOCl + H^+ + 2e^-$	—1.49
234.	$CrO_4^{--} \longrightarrow 2\ O_{2\ aq} + Cr^{++} + 4e^-$	—1.51
235.	$4\ H_2O + Mn^{++} \longrightarrow MnO_4^- + 8\ H^+ + 5e^-$	—1.52
236.	$3\ Cl^- + \underline{2\ Al(OH)_3} \longrightarrow 3\ OCl^- + 3\ H_2O + 2\ Al^{++} + 6e^-$	—1.53
237.	$2\ Cl^- + 2H^+ + \underline{PbO_2} \longrightarrow 2\ HOCl + Pb^{++} + 2e^-$	—1.53
238.	$3\ Cl^- + \underline{Mn(OH)_3} \longrightarrow 3\ HOCl + Mn^{++} + 5e^-$	—1.54
239.	$2\ Cl^- + 2H^+ + CrO_2^- \longrightarrow 2\ HOCl + Cr^{++} + 3e^-$	—1.56
240.	$3\ Cl^- + \underline{Fe(OH)_3} \longrightarrow 3\ HOCl + Fe^{++} + 5e^-$	—1.58
241.	$Cl_{2\ aq} + H_2O \longrightarrow 2\ HOCl + 2H+ + 2e^-$	—1.593
242.	$3\ Cl^- + \underline{2\ Fe(OH)_3} \longrightarrow 3\ OCl^- + 3\ H_2O + 2\ Fe^{+++} + 6e^-$	—1.616
243.	$6\ Cl^- + Sn(OH)_6^{--} \longrightarrow 6\ HOCl + Sn^{++} + 10e^-$	—1.62

TABLE 1 (*continued*)

	Oxidation reaction	E°_{25}, volts
244.	$Cl^- + \underline{Sn(OH)_2} \longrightarrow OCl^- + H_2O + Sn^{++} + 2e^-$	—1.63
245.	$4\ Cl^- + \underline{MnO_4^{--}} \longrightarrow 4\ OCl^- + Mn^{++} + 4e^-$	—1.66
246.	$2\ H_2O + \underline{MnO_2} \longrightarrow MnO_4^- + 4H^+ + 3e^-$	—1.67
247.	$\underline{Au} \longrightarrow Au^+ + e^-$	—1.68
248.	$2\ H_2O + \underline{PbSO_4} \longrightarrow \underline{PbO_2} + SO_4^{--} + 4H^+ + 2e^-$	—1.685
249.	$2\ HCO_3^- + \underline{Cu} \longrightarrow \underline{CuCO_3} + 2H^+ + 4e^-$	—1.70
250.	$2\ Cl^- + 2H^+ + \underline{MnO_2} \longrightarrow 2\ HOCl + Mn^{++} + 2e^-$	—1.71
251.	$3\ Cl^- + \underline{Cr(OH)_3} \longrightarrow 3\ HOCl + Cr^{++} + 5e^-$	—1.735
252.	$2\ H_2O + Ni^{++} \longrightarrow \underline{NiO_2} + 4H^+ + 2e^-$	—1.75
253.	$\underline{Cr(OH)_3} \longrightarrow \frac{3}{4}\ O_{2_{aq}} + Cr^{++} + \frac{8}{2}\ H_2O + 2e^-$	—1.76
254.	$2\ Cl^- + CrO_2^- \longrightarrow 2\ OCl^- + Cr^{++} + 3e^-$	—1.85
255.	$3\ Cl^- + \underline{2\ Mn(OH)_3} \longrightarrow 3\ OCl^- + 3\ H_2O + 2\ Mn^{++} + 4e^-$	—1.94
256.	$4\ Cl^- + \underline{Sn(OH)_4} \longrightarrow 4\ HOCl + Sn^{++} + 6e^-$	—1.94
257.	$4\ Cl^- + 4H^+ + CrO_4^{--} \longrightarrow 4\ HOCl + Cr^{++} + 4e^-$	—1.96
258.	$2\ Cl^- + \underline{PbO_2} \longrightarrow 2\ OCl^- + Pb^{++} + 2e^-$	—1.96
259.	$2\ HCO_3^- + \underline{2\ Ag} \longrightarrow \underline{Ag_2CO_3} + 2H^+ + 4e^-$	—2.02
260.	$4\ Cl^- + MnO_4^- \longrightarrow 4\ OCl^- + Mn^{++} + 3e^-$	—2.03
261.	$3Cl^- + \underline{2\ Fe(OH)_3} \longrightarrow 3\ OCl^- + 3H_2O + 2\ Fe^{++} + 4e^-$	—2.04
262.	$3\ Cl^- + Sn(OH)_6^{--} \longrightarrow 3\ OCl^- + 3\ H_2O + Sn^{++} + 4e^-$	—2.12
263.	$2\ Cl^- + \underline{MnO_2} \longrightarrow 2\ OCl^- + Mn^{++} + 2e^-$	—2.14
264.	$4\ Cl^- + \underline{CrO_4^{--}} \longrightarrow 4\ OCl^- + Cr^{++} + 4e^-$	—2.39
265.	$\underline{Sn(OH)_4} \longrightarrow O_{2_{aq}} + Sn^{++} + 2\ H_2O + 2e^-$	—2.39
266.	$3\ Cl^- + \underline{2\ Cr\ (OH)_3} \longrightarrow 3\ OCl^- + 3\ H_2O + 2\ Cr^{++} + 4e^-$	—2.42
267.	$2\ Cl^- + \underline{Sn(OH)_4} \longrightarrow OCl^- + 2\ H_2O + Sn^{++} + 2e^-$	—3.26

The standard oxidation potentials for half-cell reactions at other temperatures may be computed, if the free energies of the constituents are known at the desired temperatures. MacInnes[4] lists a number of experimental values for oxidation potentials at temperatures from 0°C. to 50°C., some of which show variations of less than 1% and others of which vary as much as 30% over this temperature range. Some standard potentials increase in magnitude with increase in temperature while others decrease.

[4]MacInnes, D. A., "The Principles of Electrochemistry," Reinhold Publishing Corp., 1939.

Application of Theory

The criterion for corrosion, Eq. 13, and the standard oxidation potentials may be used to examine the nature of a corrosion process, if the analysis of the water is known. All possible anodic reactions must be examined, in pairs, to determine which is the most anodic; and similarly with all possible cathodic reactions, to determine which is the most cathodic. The method is illustrated by the following examples. In order to conserve space, each reaction is referred to by the number assigned to it in Table 1, and it will be necessary to refer to Table 1 in order to follow the argument.

Example 1

Determine the conditions for the corrosion of iron in pure water at 25°C.

Solution:

Anodic reactions. From Table 1, reactions 36, 48, 65, 74 and 99 seem possible. Examining these in pairs, we have the following—

Reactions 36 and 48

$$\Delta E^{\circ}_{25} = 0.877 - 0.775 = 0.102$$

$$10^{\frac{0.102}{0.05914}} = 53$$

$$\frac{Q_{36}^{\frac{1}{2}}}{Q_{48}^{\frac{1}{2}}} = \frac{\left(\frac{1}{\alpha^{2}_{OH^-}}\right)^{\frac{1}{2}}}{\left(\frac{1}{\alpha^{3}_{OH^-}}\right)^{\frac{1}{3}}} = 1.$$

Since 1 is less than 53, reaction 36 is anodic to 48 and $\underline{Fe(OH)_2}$ may be formed at the anode, but not $\underline{Fe(OH)_3}$.

Reactions 36 and 65

$$\Delta E^{\circ}_{25} = 0.877 - 0.566 = 0.311$$

$$10^{\frac{0.311}{0.05914}} = 10^{5.25}$$

$$\frac{Q_{36}^{\frac{1}{3}}}{Q_{65}^{\frac{1}{1}}} = \frac{\left(\frac{1}{\alpha^2_{OH^-}}\right)^{\frac{1}{3}}}{\frac{1}{\alpha_{OH^-}}} = 1$$

Since 1 is less than $10^{5.25}$, 36 is always anodic to 65 and $\underline{Fe(OH)_3}$ cannot be formed at the anode until the metallic iron is completely coated with $\underline{Fe(OH)_2}$, and then only to the extent that $\underline{Fe(OH)_2}$ is capable of conducting electrons through to the metal.

Reactions 74 and 99

$$\Delta E^\circ_{25} = 0.44 - 0.036 = 0.404$$

$$10^{\frac{0.404}{0.05914}} = 10^{6.83}$$

$$\frac{Q_{74}^{\frac{1}{3}}}{Q_{99}^{\frac{1}{3}}} = \frac{(\alpha_{Fe}{}^{++})^{\frac{1}{3}}}{(\alpha_{Fe}{}^{+++})^{\frac{1}{3}}}$$

74 is at equilibrium with 99 when $\frac{\alpha^{\frac{1}{3}}_{Fe}{}^{++}}{\alpha^{\frac{1}{3}}_{Fe}{}^{+++}} = 10^{6.83}$

or when $\frac{\alpha_{Fe}{}^{++}}{\alpha^{\frac{1}{3}}_{Fe}{}^{+++}} = 10^{13.64}$.

Hence, corrosion starts with the solution of iron as both Fe^{+++} and Fe^{++}, but the equilibrium concentration of Fe^{+++} is so small that the solution of ferric iron may be ignored.

Reactions 36 and 74

$$\Delta E^\circ_{25} = 0.877 - 0.44 = 0.437$$

$$10^{\frac{0.437}{0.05914}} = 10^{7.39}$$

$$\frac{Q_{36}^{\frac{1}{3}}}{Q_{74}^{\frac{1}{3}}} = \frac{\left(\frac{1}{\alpha^2_{OH^-}}\right)^{\frac{1}{3}}}{(\alpha_{Fe}{}^{++})^{\frac{1}{3}}} = \frac{1}{(\alpha_{Fe}{}^{++}\alpha^2_{OH^-})^{\frac{1}{3}}}$$

36 is anodic to 74 when $\frac{1}{(\propto_{Fe^{++}} \propto^2_{OH^-})^{\frac{1}{2}}} < 10^{7.89}$

or when $\propto_{Fe^{++}} \propto^2_{OH^-} > 1.65 \times 10^{-15}$

or when $\propto_{Fe^{++}} > 1.65 \times 10^{13} \propto^2_{H^+}$.

Hence, for 36 to be anodic to 74, the ferrous iron in solution must exceed the following concentrations:

ppm Fe^{++}	pH
9200	7.0
92	8.0
0.92	9.0
0.0092	10.0

This criterion indicates that 74 is anodic to 36 in pure water. Corrosion starts with the solution of iron as Fe^{++} and $\underline{Fe(OH)_2}$ can be formed at the anode only at pH values greater than about 9, and then only after there is considerable iron in solution.

If the water with the corrosion products is kept in contact with the metal and H^+ is plated out as H_2 at the cathode, the pH will rise. The pH value at which 36 is at equilibrium with 74 may then be computed by noting that

$$\propto_{Fe^{++}} \propto^2_{OH^-} = 1.65 \times 10^{-15}$$

and

$$[Fe^{++}] = \tfrac{1}{2}[OH^-].$$

This computation reveals that the rate of formation of $\underline{Fe(OH)_2}$ at the anode is equal to the rate of solution of iron as Fe^{++}, when the pH value reaches about 9.18, assuming all activity coefficients are unity.

Cathodic reactions. The only cathodic reaction of importance in the corrosion of iron in pure water is 100, the plating out of H^+ as H_2 gas. The corrosion of iron in pure water is thus represented by the reactions 74 and 100:

$$\underline{Fe} + 2H^+ \rightleftarrows Fe^{++} + H_{2\,gas}$$

Reactions 74 and 100

$$\Delta E^{\circ}_{25} = 0.44 - 0 = 0.44$$

$$10^{\frac{0.44}{0.05914}} = 10^{7.43}$$

$$\frac{Q_{74}^{\frac{1}{2}}}{Q_{100}^{\frac{1}{2}}} = \frac{(\alpha_{Fe^{++}})^{\frac{1}{2}}}{\left(\frac{\alpha^2_{H^+}}{p_{H_2}}\right)^{\frac{1}{2}}} = \left(\frac{\alpha_{Fe^{++}}\, p_{H_2}}{\alpha^2_{H^+}}\right)^{\frac{1}{2}}.$$

74 is anodic to 100 when $\frac{\alpha_{Fe^{++}}\, p_{H_2}}{\alpha^2_{H^+}} < 10^{14.86}$

or when $\alpha_{Fe^{++}} < 7.2 \times 10^{14} \frac{\alpha^2_{H^+}}{p_{H_2}}$.

I. If the $H_{2_{gas}}$ is allowed to escape, so that p_{H_2} approaches zero, corrosion will be rapid at all pH values below about 9.

II. If the corrosion takes place in a closed vessel at 1 atm., the water will become saturated with H_2 and p_{H_2} will become 1 atm. Corrosion will proceed when

$$\alpha_{Fe^{++}} < 7.2 \times 10^{14}\ \alpha^2_{H^+}$$

from which the ferrous iron in solution must be less than the following:

ppm Fe^{++}	pH
4000	8
40	9
0.40	10
0.004	11

If the water containing all corrosion products is kept in contact with the metal, the pH will rise and 74 will reach equilibrium with 100 when

$$\alpha_{Fe^{++}} = 7.2 \times 10^{14}\ \alpha^2_{H^+}$$

The equilibrium pH may be computed by noting that

$$[Fe^{++}] = \tfrac{1}{2}[OH^-].$$

This computation, with activity coefficients assumed at unity, reveals that corrosion will cease in a closed vessel when the pH reaches 9.72 and the dissolved iron is about 1.45 ppm. At this point there will be a substantial coating of $\underline{Fe(OH)_2}$ on the metal, but the reaction which produces it, 36 and 100, or

$$2\,OH^- + \underline{Fe} + 2H^+ \longrightarrow \underline{Fe(OH)_2} + H_{2_{gas}},$$

has no effect on the pH or the iron in solution.

EXAMPLE 2

Determine the effect of dissolved oxygen on the corrosion of iron in pure water containing the oxygen.

Solution:

The dissolved oxygen affects only the *cathodic reactions*. From Table 1, reactions 100, 120, 160, 177, 198 and 220 seem possible at the cathode. Examining these in pairs, we have the following:

Reactions 198 and 220

$$\Delta E^\circ_{25} = -1.273 + 1.386 = 0.113$$

$$10^{\frac{0.113}{0.05914}} = 10^{1.91}$$

$$\frac{Q_{198}{}^{\frac{1}{2}}}{Q_{220}{}^{\frac{1}{2}}} = \frac{(\alpha^2{}_{H^+}[O_{2_{aq}}]^{\frac{1}{2}})^{\frac{1}{2}}}{(\alpha_{Fe^{++}}[O_{2_{aq}}]^{\frac{1}{2}})^{\frac{1}{2}}} = \left(\frac{\alpha^2{}_{H^+}}{\alpha_{Fe^{++}}[O_{2_{aq}}]^{\frac{1}{2}}}\right)^{\frac{1}{2}}.$$

198 is anodic to 220 when

$$\frac{\alpha^2{}_{H^+}}{\alpha_{Fe^{++}}[O_{2_{aq}}]^{\frac{1}{2}}} < 10^{3.82}$$

or when $\alpha_{Fe^{++}} > 1.5 \times 10^{-4} \dfrac{\alpha^2{}_{H^+}}{[O_{2_{aq}}]^{\frac{1}{2}}}$.

I. If the water is saturated with dissolved oxygen from the atmosphere, $[O_{2_{aq}}]^{\frac{1}{2}} = (0.209 \times 1.263 \times 10^{-3})^{\frac{1}{2}} = 0.1275$, and 198 is anodic to 220 when

$$\alpha_{Fe^{++}} > 1.17 \times 10^{-3}\ \alpha^2{}_{H^+}$$

from which the ferrous ions in solution must exceed

ppm Fe^{++}	pH
6.5×10^{-5}	3
6.5×10^{-7}	4

Hence 220 is cathodic.

II. If the water is only 0.01% saturated with O_2 from the atmosphere, $[O_{2_{aq}}]^{\frac{1}{4}} = (10^{-4} \times 0.209 \times 1.263 \times 10^{-3})^{\frac{1}{4}} = 0.01275$, and 198 is anodic to 220 when

$$\propto_{Fe^{++}} > 1.17 \times 10^{-2} \propto^2_{H^+}$$

from which the ferrous ions in solution must exceed

ppm Fe^{++}	pH
6.5×10^{-4}	3
6.5×10^{-6}	4

Hence it may be concluded that, when there is a measurable quantity of dissolved oxygen, reaction 220 is cathodic and no water is formed.

Reactions 120 and 220

Examination of this pair shows that it is controlled by the same criterion as the pair 198 and 220, and 220 is cathodic.

Reactions 160 and 220

$$\Delta E^\circ_{25} = -0.882 + 1.386 = 0.504$$

$$10^{\frac{0.504}{0.05914}} = 10^{8.52}$$

$$\frac{Q_{160}^{\frac{1}{4}}}{Q_{220}^{\frac{1}{4}}} = \frac{(\propto_{Fe^{++}} [O_{2_{aq}}]^{\frac{1}{4}})^{\frac{1}{4}}}{(\propto_{Fe^{++}} [O_{2_{aq}}]^{\frac{1}{4}})^{\frac{1}{4}}} = \frac{1}{[O_{2_{aq}}]^{\frac{1}{4}}}$$

160 is anodic to 220 when $\frac{1}{[O_{2_{aq}}]} < 10^{68.2}$

or when $[O_{2_{aq}}] > 10^{-68.2}$.

Hence $\underline{Fe(OH)_3}$, instead of $\underline{Fe(OH)_2}$, is formed at the cathode.

Reactions 177 and 220

Examination of this pair indicates that 177 is anodic when

$$\alpha_{Fe^{++}} > 1.5 \times 10^{-4} \frac{\alpha^2_{H^+}}{[O_{2_{aq}}]^{\frac{1}{2}}}$$

the same criterion as for the pair 198 and 220. Hence, $\underline{Fe(OH)_3}$ will not be dissolved from the cathode until the oxygen is exhausted.

Reactions 100 and 220

$$\Delta E^\circ_{25} = 0 + 1.386 = 1.386$$

$$10^{\frac{1.386}{0.05914}} = 10^{23.4}$$

$$\frac{Q_{100}{}^{\frac{1}{2}}}{Q_{220}{}^{\frac{1}{2}}} = \frac{\left(\frac{\alpha^2_{H^+}}{p_{H_2}}\right)^{\frac{1}{2}}}{(\alpha_{Fe^{++}}[O_{2_{aq}}]^{\frac{1}{2}})^{\frac{1}{2}}} = \left(\frac{\alpha^2_{H^+}}{\alpha_{Fe^{++}} p_{H_2}[O_{2_{aq}}]^{\frac{1}{2}}}\right)^{\frac{1}{2}}.$$

100 is anodic to 220 when

$$\frac{\alpha^2_{H^+}}{\alpha_{Fe^{++}} p_{H_2}[O_{2_{aq}}]^{\frac{1}{2}}} < 10^{46.8}$$

or when $p_{H_2}\alpha_{Fe^{++}} > 1.6 \times 10^{-47} \frac{\alpha^2_{H^+}}{[O_{2_{aq}}]^{\frac{1}{2}}}$.

At the start of corrosion, both p_{H_2} and $\alpha_{Fe^{++}}$ are zero. Hence, corrosion starts 74 and 100 to produce Fe^{++} and $H_{2_{aq}}$. When $p_{H_2}\alpha_{Fe^{++}}$ exceeds the above value, 220 becomes cathodic to 100 and corrosion continues 74 to 220. If the water is only 0.01% saturated with O_2 from the air, $[O_{2_{aq}}]^{\frac{1}{2}} = (10^{-4} \times 2.64 \times 10^{-4})^{\frac{1}{2}} = 2.07 \times 10^{-6}$, and the equilibrium values of $p_{H_2}\alpha_{Fe^{++}}$ are

$p_{H_2}\alpha_{Fe^{++}}$	pH
7.7×10^{-45}	2
7.7×10^{-47}	3
7.7×10^{-49}	4
7.7×10^{-55}	7

Hence, under the most favorable conditions, low pH and low $\propto_{Fe^{++}}$, p_{H_2} must be extremely small for hydrogen to be evolved at the cathode. For example, if $\propto_{Fe^{++}} = 10^{-7}$ (0.0058 ppm) and the pH is 2, the partial pressure of hydrogen must be less than 7.7×10^{-38} atm. In the presence of measurable quantities of dissolved oxygen, therefore, corrosion proceeds 74 to 220; and no hydrogen is evolved at the cathode, unless it is liberated as fast as it is formed, so as to maintain the partial pressure of H_2 at practically zero.

Reactions 74 and 220

The principal reactions, therefore, in the corrosion of iron in pure water containing oxygen are 74 at the anode and 220 at the cathode, as follows:

Anode: $\underline{Fe} \longrightarrow Fe^{++} + 2e^-$

Cathode: $\underline{Fe(OH)_3} \longleftarrow \frac{3}{4} O_{2_{aq}} + Fe^{++} + \frac{3}{2} H_2O + 2e^-$

The whole-cell reaction is:

$$\underline{Fe} + \frac{3}{4} O_{2_{aq}} + \frac{3}{2} H_2O \longrightarrow \underline{Fe(OH)_3},$$

which does not involve a change in pH. The reaction proceeds until the protective coating $\underline{Fe(OH)_3}$ insulates the cathode or until the $O_{2_{aq}}$ approaches exhaustion.

$$\Delta E^\circ_{25} = 0.44 + 1.386 = 1.826$$

$$10^{\frac{1.826}{0.05914}} = 10^{30.9}$$

$$\frac{Q_{74}^{\frac{1}{4}}}{Q_{220}^{\frac{1}{4}}} = \frac{(\propto_{Fe^{++}})^{\frac{1}{4}}}{(\propto_{Fe^{++}}[O_{2_{aq}}]^{\frac{3}{4}})^{\frac{1}{4}}} = \frac{1}{[O_{2_{aq}}]^{\frac{3}{4}}}$$

Corrosion should proceed until $\frac{1}{[O_{2_{aq}}]^{\frac{3}{4}}} = 10^{30.9}$

or until $[O_{2_{aq}}] = 10^{-82.3}$.

It should be noted, however, that reaction 100 will become cathodic long before this concentration of dissolved oxygen is reached.

Hence, if the protective coating of $\underline{Fe(OH)_3}$ does not stop corrosion before the oxygen is reduced to about 10^{-60}, corrosion will continue 74 and 100 with the evolution of H_2 and the pH will rise to equilibrium at 9.72 with about 1.45 ppm of Fe^{++} in solution.

Protective Coatings

It will be noted in Figure 1 that a Type I reaction at the anode is favorable to corrosion, since no solid deposit is formed at the anode as with Type II and Type III reactions. The continuance of the corrosion process with Type II and Type III anodic reactions depends upon the value of the deposit as a *protective coating*. It has already been shown that a protective coating of $\underline{Fe(OH)_2}$ will not be formed on iron, unless the pH value of the solution exceeds 9. It may be shown that a protective coating of $\underline{Al(OH)_3}$ will form on aluminum at the anode at pH values between 4.5 and 8. Below pH 4.5, aluminum corrodes as Al^{+++} in a Type I anodic reaction and, above pH 8, aluminum corrodes as $H_2AlO_3^-$ in a Type II anodic reaction.

It will also be noted in Fig. 1 that a Type I reaction and certain reactions of Types IV and V at the cathode are favorable to corrosion, since no insulating deposit is formed. Certain Type IV and Type VI reactions at the cathode cause deposits and the effectiveness of these deposits in insulating the metal will determine their value as protective coatings in stopping corrosion. It has already been demonstrated that $\underline{Fe(OH)_3}$ is formed at the cathode on iron in the presence of even a trace of dissolved oxygen. No water is formed at the cathode in the corrosion of iron, unless there is no iron in solution.

In the plating-out of hydrogen at the cathode in acid solutions, the gas forms a momentary insulating film, which is removed as each gas bubble is released from the interface. An excess of voltage called the *hydrogen overvoltage* is required to cause this cathodic reaction to proceed rapidly.

PROCEEDINGS

February 1946 Meeting

Hotel Statler, Boston, Mass.

Thursday, February 28, 1946

President Harold W. Griswold in the Chair.

Secretary Conroy announced that the following had been elected to membership by the Executive Committee:

Members: George N. Watson, Superintendent of Water Department, Braintree, Mass.; Angelo Iantosca, with Massachusetts Department of Public Health, Boston, Mass.; Paul M. Nickerson, Water Works Engineer, Hampden, Me.; James P. McCarthy, Water Plant Operator, Wickford, R. I.; Asa H. Copeland, Superintendent of Water Department, Tiverton, R. I.; Harry P. Danaher, Water Works Engineer, Thomaston, Conn.; Charles J. Knoener, New England District Manager of Pitometer Co., New York, N. Y.; Oscar V. E. Jansa, Consulting Engineer, Stockholm, Sweden.

Associate: R. E. Chapman Co., water well drilling, Oakdale, Mass.

Chairman E. Sherman Chase of the Committee on Reciprocal Relations with the Institution of Water Engineers made a brief announcement relative to the work of the committee. He stated that Past-President Karl R. Kennison had prepared an exchange paper, entitled "Water Supply Developments in Boston, Massachusetts, and Recent Additions to the Works", which was presented at a meeting of the Institution of Water Engineers in December, 1945. This paper, together with abstracts of the discussions, was published in the winter number of Water and Water Engineering. Mr. Chase also announced that the committee has made tentative arrangements for Harvey B. Kinnison to contribute another exchange paper, dealing with the work of the Geological Survey in its hydrological division.

A paper, "Water Supply Practice in Germany—1945", was read by Arthur E. Gorman, Consultant, Office of Surplus Property Utiliza-

tion, formerly Director, Water Division, Office of War Utilities, War Production Board, Washington, D. C. After presenting this paper, Mr. Gorman spoke on the opportunity for municipal water works to purchase surplus property and on the opportunity for the water works industry to coöperate in supporting the housing program.

Lieutenant John F. Kennedy, U.S.N.R., of the American Red Cross Speakers' Bureau, speaking on behalf of the Red Cross War Fund, related some of his experiences in World War II.

A paper, "The Development of Plastic Coatings for Corrosion Protection in the Water Works Industry", was read by Arthur B. Smith, Amercoat Division, American Pipe and Construction Co., Chicago, Ill.

March 1946 Meeting

Hotel Statler, Boston, Mass.

Thursday, March 21, 1946

President Harold W. Griswold in the Chair.

Secretary Conroy announced that the following had been elected to membership by the Executive Committee:

Members: Gordon C. Tower, Superintendent and Chemist, Presque Isle Water District, Presque Isle, Me.; James F. Shurtleff, Town Manager and Manager of Municipal Water Department, Mansfield, Mass.; Donald B. Stevens, U. S. Public Health Service, Newburyport, Mass.; Charles B. Perkins, President and Manager of Kingston Water Co., Wakefield, R. I.; Harry W. Kendrick, Superintendent of Water Department, Shelburne Falls, Mass.; Emery S. Littlefield, Jr., Superintendent and General Manager, Sanford Water District, Alfred, Me.; Carl H. Bergman, with Wallace & Tiernan Co., Auburndale, Mass.; Columbus G. Carley, Superintendent, Searsport Water Co., Searsport, Me.; Arthur W. Lawton, Clerk and Secretary, Torrington Water Co., Torrington, Conn.; Peter C. Karelekas, Chief Water Engineer, Springfield Water Works, Springfield, Mass.; Clarence K. Dion, Superintendent and Engineer, Water Department, Westerly, R. I.; Edwin S. Evans, Chief Engineer, Dedham Water Co., Medfield, Mass.; Frank C. Barrows, Chemist, Bridgeport Hydraulic Co.,

Bridgeport, Conn.; Edmund C. Sanderson, Water and Sewer Commissioner, Winchester, Mass. (Reinstated).

Associate: Utilities Supply Corp., water works supplies, Boston, Mass.

Upon motion of Sidney S. Anthony, duly seconded, it was voted that Past-Presidents Kingsbury, Carlton, Shaw, Sampson and Scott be appointed to the Nominating Committee.

Upon motion of William W. Brush, duly seconded, it was voted that the Association appoint a representative to present its views on control of stream pollution, whether by the federal government entirely or by the state agencies with the advice of the Public Health authorities.

It was then voted, upon motion of Leonard W. Trager, duly seconded, that Warren J. Scott represent the Association.

Upon motion of E. Sherman Chase, duly seconded, it was voted that the New England Water Works Association pay the expenses of their representative to this hearing in Washington.

It was then voted, upon motion of Warren J. Scott, duly seconded, that the Association go on record as favoring control of stream pollution by the states in coöperation with the United States Public Health Service, rather than to have it all under federal control.

A paper, "Metropolitan Water District Financing and the Cost of Metropolitan Water," was read by Karl R. Kennison, Chief Engineer, Metropolitan District Water Supply Commission, Boston, Mass.

A paper, "Vocational Rehabilitation of Veterans and Disabled Veterans Training-on-the-Job," was read by George P. Capen, Training Officer, Veterans Administration, Boston, Mass.

A paper, "Organic Coatings in Water Works Maintenance," was read by D. R. Meserve, Manager of Technical Service for Organic Coatings Division, United Chromium, Inc., Waterbury, Conn.

A colored movie, "Copper and Its Alloys", was shown through the courtesy of Revere Copper and Brass, Inc., New Bedford, Mass.

Superintendents' Round Table

February 28, 1946

Kenneth H. Damren of the Massachusetts Retirement Appeal Board presented the subject of "Retirement for Municipal Employees." He reviewed the history of State retirement acts from the State contributory system, started in 1912, to and including the latest revisions or amendments passed in 1945.

The 1945 Legislature amended and liberalized the contributory retirement laws relating to employees of the Commonwealth and its political subdivisions, to become effective January 1, 1946, and to apply to all employees who are members of the retirement system on that date or who become members thereafter. Commencing January 1, 1946, deductions for the retirement system will be five per cent of the employee's total regular compensation and will no longer be limited to five per cent of the first $2,600 of regular annual compensation. This will affect only those employees whose regular annual compensation is in excess of $2,600. Their retirement allowances will be increased because of the additional deductions which they will make.

The member now has a choice of one of three options under which his retirement allowance may be paid. The new formula for determining the amount of retirement allowance is simpler, more easily understood and will generally give substantially larger allowances than the present formula. Benefits payable for ordinary disability and accidental disability and in case of death, resulting from an accident occurring while in performance of duty, are included in the new law.

This new retirement law, Chapter 658 of the Acts of 1945, is of vital interest to all municipal employees and should be carefully studied, in order that the individual may be able to obtain the greatest benefits from it.

This instructive meeting was sponsored by Nelson A. Boardman, Assistant Superintendent of the Water and Sewer Board, Danvers, Mass.

C. Roger Pearson

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Consulting Sanitary Engineer

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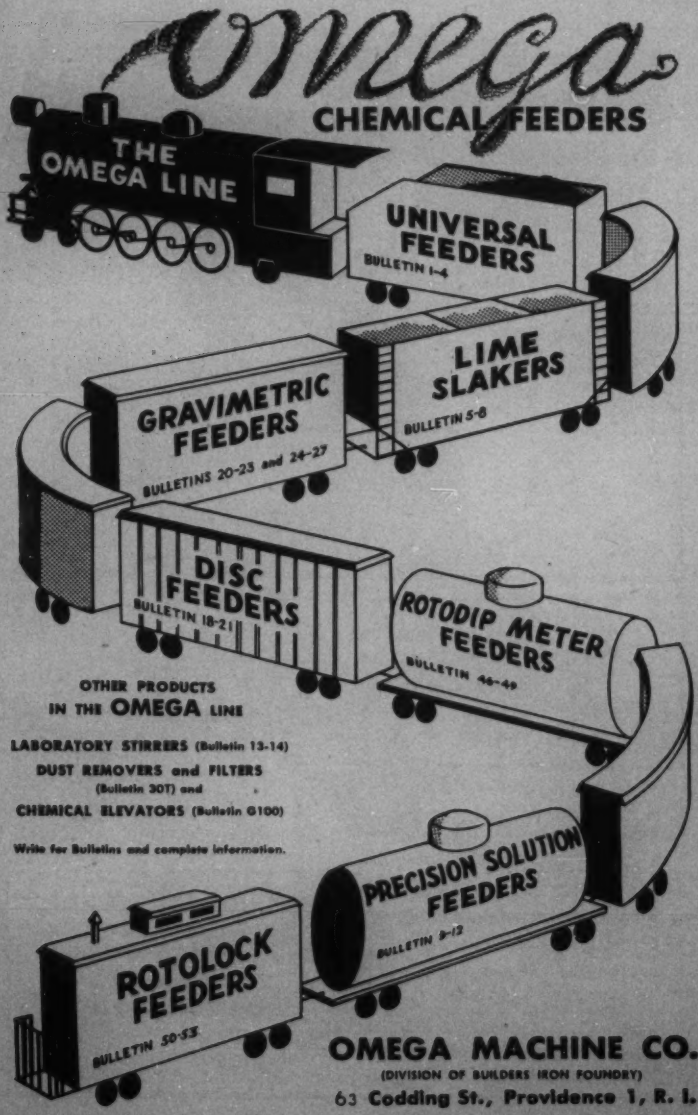

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For all your Trident Meters, whether new or old, you need carry only one set of repair parts—the newest. The resultant economy in parts inventory, in the amount of storage space required, and in the records necessary to keep track of them, is an item which no Water Department should overlook.

137

Danvers Demonstrates

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1	— 24	1" Disc Chambers
3	— 70	Registers
3	— 48	¾" Disc Chambers
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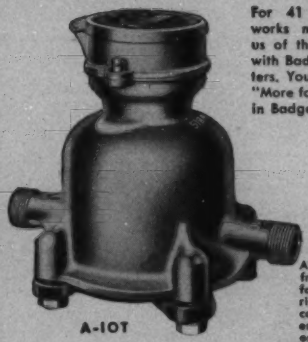
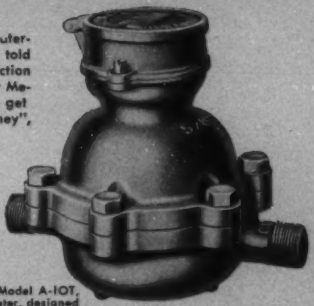


A-IOT



SC-IOT

Above, left, Model A-IOT, frost proof meter, designed for cold climates. Above right, Model SC-IOT, (split case), designed for warmer climates. Oil enclosed or open type gear trains are optional.

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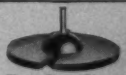

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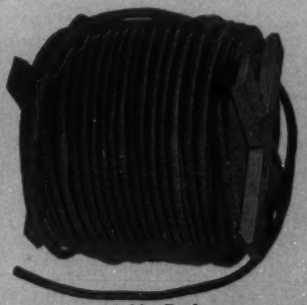

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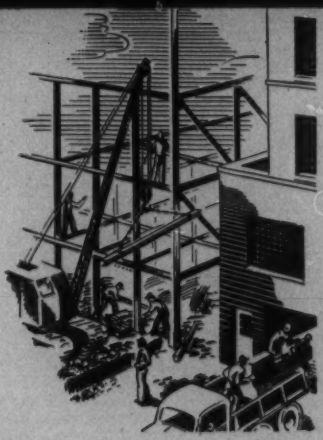

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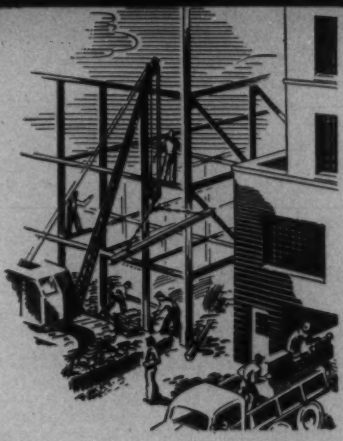

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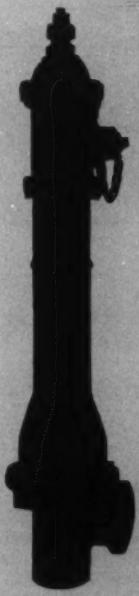

Distinctive Features of the EDDY Valves

ONLY three parts are moved by the Stem—the ball and the two gates. Each gate is hung from one of the trunnions on the ball. A convex surface at the base of each trunnion fits a concave surface on the back of the gate. This allows the gates to adjust themselves properly to their seats. . . . The gates, being free to revolve on the trunnions, do not always seat in the same position. Gates are center bearing and adjustable. They are forced to their seats with equal pressure at all points. There are two hooks on the ball on sizes 4-inch and larger, which loosely engage with the gates.

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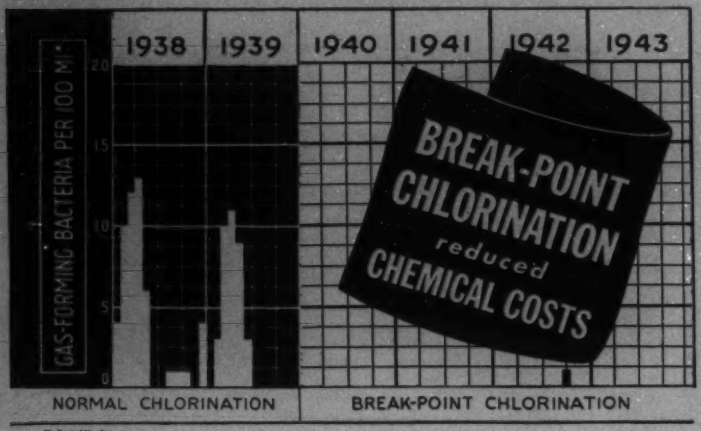
Besides valves and hydrants to meet the most exacting demands of waterworks service, the complete EDDY Line includes: valves for sewage disposal works; valves for steam, gas and oil; check valves, foot valves, plug valves, shear gates, indicator posts, etc. EDDY valves are made in three classes: Iron Body Bronze Mounted, All Bronze, and All Iron Valves.

Eddy Valve Co.

WATERFORD NEW YORK



...and cut gas-formers 99.2%

Charted above is half of a double-barreled story of Break-Point Chlorination in action.

First, improved coagulation and longer filter runs resulted in a saving in chemical costs of ten cents per million gallons treated. And second, the *free available chlorine residuals* maintained throughout the system by Break-Point Chlorination reduced gas-formers in the finished water 99.2%.

This case shows what Break-Point Chlorination can accomplish. Call your Wallace & Tiernan Representative today for further details. He'll be glad to show you from actual experience — how it can give your community a safer water — often at lower cost.

BACTERIOLOGICAL DATA

	NORMAL CHLOR.	B-P CHLOR.	CHANGE
Total Bact. per ml (avg.)			
Raw	588	399	—32.1%
Filtered	1	1	0
Finished	1	1	0
I.M. (Indicated Number) Gas-Forming Organisms per 100 ml			
Raw	70.00	53.07	— 7.0%
Filtered	.89	.01	—97.7%
Finished	.38	.003	—99.2%

"The Only Safe Water is a Sterilized Water"

WALLACE & TIERNAN COMPANY, INC.

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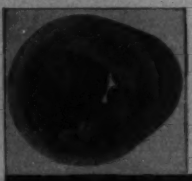

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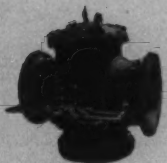

Controls elevation of water in tanks, basins and reservoirs

ALTITUDE VALVE

1. Single Acting
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A self contained unit, with three or more automatic controls

COMBINATION VALVE

Combination automatic control both directions through the valve.

Maintains desired discharge pressure regardless of change in rate of flow

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Maintains safe operating pressures for conduits, distribution and pump discharge

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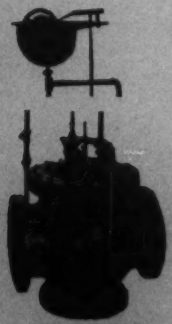

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1. As direct acting

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FLOAT VALVE

Electric remote control—solenoid or motor can be furnished

REMOTE CONTROL VALVE

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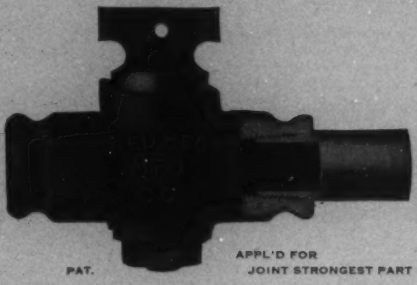

Fig. 220

Tee Head Recessed Stop and Waste

RED HED MFG. CO.

Is a New England Manufacturing concern, owned and operated by New England men who have had more than a half century of close association with Water Works Superintendents, Managers and Engineers.

During our twenty-four years of existence of RED HED MFG. CO. it has been our constant aim to manufacture the best Water Works brass goods we could make.

We manufacture but one quality of Water Works brass goods. We have no second grade to offer.

Experience has proven that RED HED brass goods have given better service with less maintenance cost and a minimum amount of annoyance, trouble and expense in the matter of replacements.

RED HED MFG. CO.

Manufacturers of

RED HED Brass Goods for Water Works

368 Congress Street Boston, Mass.

DESCRIPTION

%Proportioneers% Duplex Chem-O-Feeder is a constant rate of feed duplex diaphragm pump with two reagent heads for feeding one or two liquids. The unit is provided with standard "See-Thru" plastic reagent heads and the feed of each pump is manually adjustable while pump is operating by means of stroke length adjustment knob. The mechanism is enclosed in an oil bath and the stroking arrangement is designed for feeding an almost constant stream. This unit is provided with ¼ HP or ¼ HP motor for feeding against positive pressures of up to 100 lbs. per square inch.

CHEMICALS HANDLED

Calcium and sodium hypochlorite — aqua ammonia — aluminum sulphate — sodium carbonate — lime slurry — caustic — carbon slurry — ferric chloride — ferric sulphate, etc.

SPECIFICATIONS

(per pump head)

Stroke length . . . . . 0 to 0.25"
Delivery per stroke . . 0 to 9.5 cc (at 10 lbs.)
0 to 8.3 cc (at 100 lbs.)
Stroking rate . . 17, 32, 57 strokes per minute
Maximum capacity . . . 8.6 GPH (at 10 lbs.)
7.5 GPH (at 100 lbs.)
Maximum operating pressure —
125 lbs. per sq. inch. for intermittent duty
100 lbs. per sq. inch. for continuous duty
Maximum chlorine feed per 24 hours using 12½% sodium hypochlorite solution . 200 lbs.

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Water Plants (municipal and private) • Swim Pools (municipal and private) • Bottling Plants, Bleacheries • Oil Producers (secondary recovery) etc.

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Gross weight . . . . . 140 lbs.
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No. 6 in a series

Formula for City Growth

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Graver Iron Removal and Softening System installed in an Indiana municipality.

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With this equipment iron is removed from the entire water supply either by aeration or by passing the water thru basic exchange units. After oxidation in an aerator the water is delivered to filters for the filtering out of the formed iron precipitate. A portion of the water is then passed thru Graver Zeolite Softeners and softened to zero hardness. The final effluent from the zeolite softeners is blended with the iron-free raw water to produce any desired degree of hardness. The water thus produced is ideal for municipal use, being iron-free and soft.

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SINCE 1866

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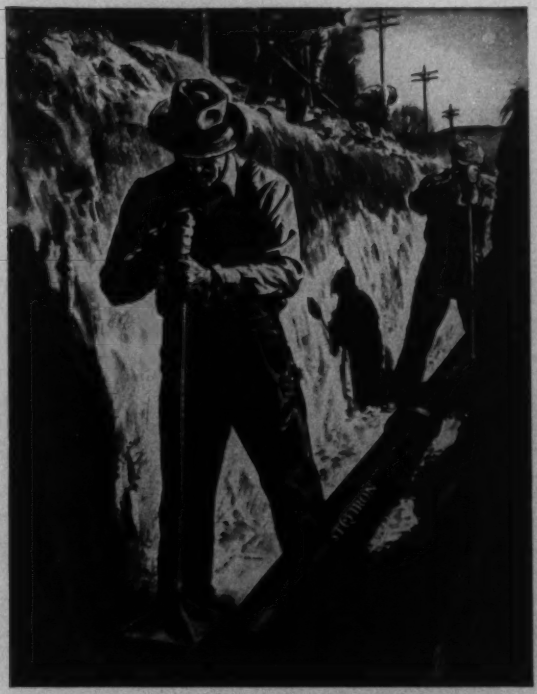

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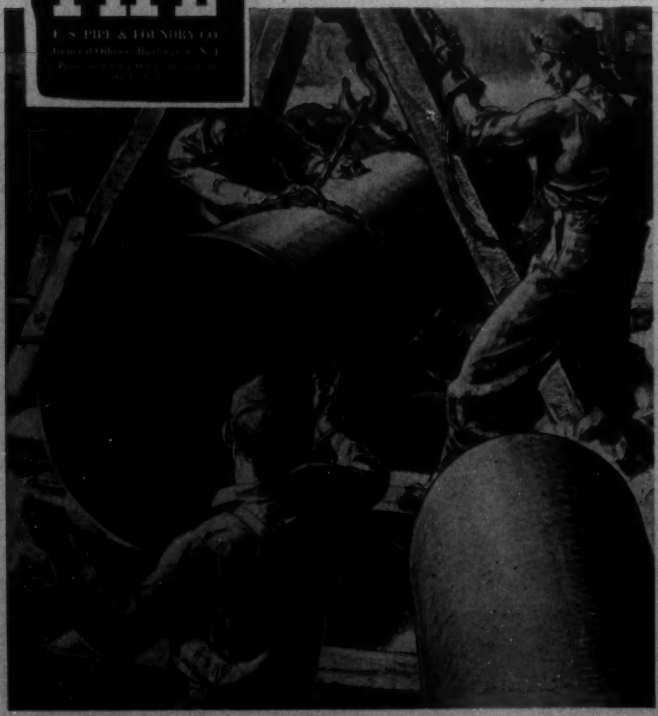

The Journal of the New England Water Works Association

is a quarterly publication, containing the papers read at the meetings, together with reports of the discussions. Many of the contributions are from writers of the highest standing in their profession. It affords a convenient medium for the interchange of information and experience between the members, who are so widely separated as to find frequent meetings an impossibility. Its success has more than met the expectation of its projectors; there is a large and increasing demand for its issues, and every addition to its subscription list is a material aid in extending its field of usefulness.

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